Norman F. H. Brady

DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

Mines Branch Program
on Environmental Improvement

THIRD MINES BRANCH SEMINAR ON ENVIRONMENTAL IMPROVEMENT

by

THE STAFF

Report ADM 72-2

MARCH, 1972

90-04496/

AGENDA AND CONTENTS

THIRD MINES BRANCH SEMINAR ON ENVIRONMENTAL IMPROVEMENT

February 18, 1972

THEME: TOWARD POLLUTION-FREE MINERAL AND ENERGY PROCESSES

PROGRESS IN 1971

			Page
1.	MINES BRANCH ENVIRONMENTAL IMPROVEMENT ACTIVITY	Dr. John Convey	1
2.	CHAIRMAN'S REMARKS	E.R. Mitchell	4
3.	MINES BRANCH CONTRIBUTIONS TO ENVIRONMENTAL IMPROVEMENT:		
	FUNDAMENTALS		
	3.1 Kinetics of Formation and Removal of SO_2 and NO_x	Dr. R.C. Kerby	8
	3.2 The Mathematical Modelling of Plume Dispersion	Dr. H. Whaley	13
	3.3 New Analytical Techniques:		
	3.3.1 Analysis of Sulphur in Oil and Coal by X-Ray Fluorescence Techniques	Dr. D.S. Montgomery	20
	3.3.2 The Carle Thermal Analysis System for Detection of Trace Qualities of Hydrocarbons	Dr. M.L. Boyd	21
	3.3.3 Investigation of Sulphur Compounds in Crude Oils	Dr. H. Sawatzky	22
	3.3.4 Development of Methods for Determining Sulphur, Heavy Metals, Oil, and Water in Coals and Coal Products	Dr. B.J. Whalley, S.M. Ahmed, W.R. Leeder.	26

		Page
EXPERIMENTAL		
3.4 Mine Air Quality-Dust and Radiation	T.S. Cochrane	31
3.5. Summary of Diesel Investigation Facility Progress During 1971	E.D. Dainty, J.P. Morgan.	35
3.6. Detailed Measurements of Emissions from Six Cupolas	Dr. R. Warda, R.K. Buhr	40
ADVANCED PROCESS RESEARCH		
3.7 The Desulphurization of Oil Before Combustion	Dr. B.I. Parsons	45
3.8 CCRL Fuel Efficiency Program	E.R. Mitchell	49
3.9 Flame Research		
3.9.1 Blue Flame	Dr. T.D. Brown	53
3.9.2 Low NO_x Flames	Dr. T.D. Brown G.K. Lee	55
3.9.3 The Combustion of Coal-in-Oil Slurry	G. K. Lee	59
3.9.4 Next Generation of Burners	F.D. Friedrich	61
3.9.5 Flame and Air Pollution Research Bibliography	CCRL Staff	66
3.10 New Hydro-Metallurgical Processes	H.M. McCreedy	72
3.11 Chlorination Processes - Phase Equilibrium Studies in the (Fe, Co, Ni) -S- Cl Systems	Dr. A.H. Webster	75
IMPROVEMENTS TO PROCESSES		
3.12 Reduction of Toxic Dusts from Pyro-Metallurgical Processes	G.E. Viens	79
3.12.1 Coal Carbonization and Related Studies	J.C. Botham	84

IMPROVEMENTS TO PROCESSES (Continued)		Page
3.12.2 Utilization of Discarded Automobile Tires in Coke-Making Operations	W.R. Leeder	90
3.12.3 New Metallurgical and Coal Beneficiation Processes	Dr. J.H. Walsh	91
3.13 Re-Use of Mineral Wastes	R.K. Collings	94
3.14 Reduction of Pollution from Mine Wastes		
3.14.1 Ion Exchanges and Neutralization Studies for Pollution Abatement of Acid Mine Drainage Waters	A.J. Gilmore	100
3.14.2 An Experimental Study of the Weathering of Mill Tailings	Dr. A. Jongejan	105
3.14.3 Adsorption of Trace Quantities of Metal Ions by Clay Minerals	Dr. H.F. Steger	110
3.15 Revegetation of Mines Wastes	T.S. Cochrane	115
3.16 Progress with Problems of Coal Mine Refuse Banks	T.E. Tibbetts	118
3.17 LITERATURE REVIEWS		
3.17.1 The Clean Fuel Gas Concept in a Combined Gas Turbine-Steam Turbine Power Plant	Dr. W.A. Herrmann	120
3.17.2 Methods for the Removal of Sulphur Dioxide from Waste Gases	Dr. H.P. Gibbs	125
3.18 Committee Activites		126
4. DISCUSSION - The Next Seminar		128

THE THIRD MINES BRANCH SEMINAR ON ENVIRONMENTAL IMPROVEMENT

THEME - TOWARD POLLUTION-FREE MINERAL AND ENERGY PROCESSES

1. THE MINES BRANCH ENVIRONMENTAL IMPROVEMENT ACTIVITY

by

John Convey

Welcome

I would like to welcome you, ladies and gentlemen, to this seminar, the third of the series, in which we will describe our contributions to the control of pollution from heat process sources.

We live in a technological age. Indeed, our urban communities are a technological "ensemble" where heat, energy and metals are combined to pump our water, process our sewage and provide us with transportation, food and an array of services and luxuries that were unheard of 30 years ago. It is the basis of this technology that we will examine to-day.

Environmental Improvement Activity

This activity is somewhat unique if only for the fact that it is a first attempt at developing a significant program on a Branch basis. It was inaugurated in 1970 to highlight the important pollution aspects of the Mines Branch research which, historically, had not been separated from other research parameters, either in project planning or in publications. The Environmental Improvement Activity was conceived, therefore, as a means of systematising the research, engineering, and technological expertise of individuals spread throughout the Branch in many disciplines, and to document their contributions to the objectives described in the following.

Objective

Enviromental protection and improvement.

Sub-Objectives

Enviromental Improvement

Reduce air, water and land pollution arising from mining and metallurgical operations, including the conversion of energy minerals.

Sub-Sub-Objectives

1. Prevent or abate pollution at source.
2. Disperse or dispose of effluents to tolerable levels.
3. Re-use wastes and residues.

Sub-Activities	Responsibility Centres
1. Characterization of pollutants at source of heat raising processes using fossil fuels on their own or in combination with minerals, concentrates, and metals. Research on hydrometallurgical and other substitute pollution-free processes. Determination of potential mineral and metal pollutants.	FRC, MREC, PM, MS, EM
2. Research on treatment, dispersion and disposal of effluents.	FRC, MREC, EM, MP, PM
3. Research on re-use processes for wastes and residues.	FRC, MREC, EM, MP, MS
4. Development of control methods for pollution, including the development of a diesel engine testing facility.	FRC, MRC

How the Program is Managed

It was intended that the program be as informal as possible in its early development stages. However, it works through an Environmental Improvement Committee which reports to me.

The committee organization is as follows:

Co-chairmen	-	E.R. Mitchell
	-	F.T. Rabbitt
Members	-	N. Banks
	-	J.C. Botham
	-	T.S. Cochrane
	-	J.O. Edwards
	-	W.A. Gow
	-	G.K. Lee
	-	D.E. Pickett
	-	A.H. Webster
Associate	-	J.W. Schmidt, D.O.E.

How the Program Functions

The reduction and control of pollution has been singled out as the subject of highest priority in all of the Mines Branch activities. Since it is a subject that cuts across many disciplines, it is expected that there will be an acceleration of inter-disciplinary collaboration in research projects.

The program was inaugurated by bringing people together, who have a common interest in the program objectives, at a Mines Branch Seminar on January 8 and 9, 1970. This first seminar was devoted to establishing an inventory of Branch's expertise and a continuing inventory of pollutants which are discharged from the previously designated processes.

The second seminar, held on November 17, 1970, was planned to summarize Mines Branch contributions to pollution abatement during the year 1970.

Your chairman will explain to-days agenda and I trust that you will profit from it.

2. CHAIRMAN'S REMARKS

by

E.R. Mitchell

For the benefit of visitors and those who are not familiar with this series of seminars, it should be explained that our seminars are a forum for communicating; for researchers to communicate with researchers; for researchers to communicate with headquarters; and for researchers to communicate with their colleagues in other departments. In communicating, it is the intention to explain the significance and relevance of the Mines Branch programs in relation to environmental improvement and their contributions to innovation which is the Branch's end product and claim to fame.

Although we publish in numerous journals, we have reason to doubt that our colleagues at home have a reasonable understanding of what we are doing. Therefore, we thank our visitors for taking time to be here and we will reward them with a lot of sound information in a short time.

To-day's agenda may seem to our visitors to be a "far-out" jumble and the contents of the pre-printed abstracts may seem to be further out. But, it may be worth pointing out that we speak to-day from a background of some 10,000 man-years of accumulated experience which is an unequalled source of information on Canadian mineral and heat processes and their impact on the environment. Indeed, our pollution inventories are not extrapolations of inventories from the United States as a recent press release charged.

To bring to-day's subjects into focus in one paragraph I would remind you that as recently as 70 years ago, sulphide ore was pile roasted, a practice that virtually devastated the Sudbury and Trail areas. No one approved of either the practice or the land damage, but they were tolerated because the environment was known to be cruel, even a man killer, and in order to survive, our predecessors saw the need for more technology, i.e. more heat and mineral processes. Then came the reverberatory furnace; even with the early and primitive pulverized-coal firing system, it was a dramatic

improvement over pile roasting for copper and nickel extraction because it produced less pollution and provided for the discharge of off-gases through a chimney, high above ground level. Other fuel-fired smelter furnaces were equally dramatic developments in their time, including the open hearth, the shaft furnace such as the cupola and multideck shaft furnace, the converter, the electric furnace, the crucible furnace and others which do not fit any particular category such as the electric-arc crucible furnace. Continual improvements have been made over the years through innovative research, such as that done at the Mines Branch, and the result has been less pollution per unit of heat and mineral production. But, there has been a demand for more heat and more metals for more technology for more people, as Dr. Convey said previously, and this has placed more pressure on researchers for more innovation.

Having said that, what is the significance of this trend to EM&R and to the Nation? Clearly it is driving us rapidly to an energy crisis. Indeed, the most dramatic fact that has emerged from both my pollution inventories and energy studies by others is the lavish use of fuel and energy which has become an apparently irreversible way of life. The annual rate of energy consumption and export (fuels and electricity) continues to increase at an accelerated rate which bears no relationship to the magnitude of fuel resources. It is much like supplying fuel to a diesel locomotive from a 45 gallon drum. Surely, the locomotive together with the load it must pull will stall down the track within our sight if additional energy is not there to be picked up.

Considering our National indigenous fuel supply, experts (Professor Ryan, University of Alberta for one) have warned that the low-cost gas and petroleum will come to an end in 5 or 6 years and after that, the more distant and costly sources will start to fill our needs. When the time comes that we are dependent on Arctic and off-shore gas and petroleum for part of our fuel needs, then we may not be far from returning to coal as the principal source of energy. It is not known when this will be but if it is 30 years hence, we do not have adequate time as of now to prepare for such an eventuality. Therefore, most of us are inclined to think optimistically and to trust to either luck or magic technology to save us. In any case, it can

do no harm to do some serious thinking and to consider implementing a range of strategies. Obviously there has been a great deal of thinking about the future energy crisis. This is evident from the seeming urgency of fuel exploration programs but the search for more natural gas and petroleum has not been balanced with appropriate programs for rationalizing energy conservation. Thus, it seems most constructive for us to examine strategies relative to fuel selection and energy conservation. In doing so, it is difficult to discuss short and long term strategies separately because they have strong interdependence.

The nuclear fission reactor is probably the most dramatic (and costly) strategy to be implemented in Canada for supplementing indigenous energy resources, but it is becoming increasingly evident that it may not be an adequate solution in either the short or long term. Its problems in the short term (as a means for extending fuel resources) are well known. In the long term, generations in the future may require such massive amounts of energy that they must depend upon the fusion reactor, but, it may be 100 years away if knowledge only doubles every 10 years. Even if it is 50 years away as some optimists believe possible, there still looms an energy crisis just the same.

If there is any truth to this, then there is a need to protect the nation's fuel supply for the next 50 or 100 years. Surely we should not deliberately deplete natural gas and petroleum resources as quickly as possible simply because they are convenient, but instead we should make them span as many of the next 100 years as possible.

This is why I react to the pressures of environmental protection agencies which force a power utility to burn <u>natural gas</u> and <u>crude oil</u> instead of coal in thermal power stations. This fuel manipulation serves only to avoid solving the pollution problem from burning coal and helps to precipitate the energy crisis which looms on the hazy horizon.

These are just a few of the reasons for selecting the subjects on this agenda. The Mines Branch reports and papers published during the past year attest to the large volume of material that could be included. It is also evident, that year by year, innovation requires more inter-disciplinary scientific input and this is reflected in the subjects of this seminar.

It is regretted that time cannot be given to a literature review by Dr. H.P. Gibbs entitled "Methods of Removal of SO_2 from Waste Gases" and other important work but we expect the readers of our proceedings volume to refer to either individual authors or to members of the Mines Branch Environmental Committee for any additional information that may be required.

3.1 - KINETICS OF FORMATION AND REMOVAL OF SO_2 AND NO_x

by

R. C. Kerby

- - - -

ABSTRACT

(1) Lime Utilization in SO_2 Scavenging (P. Marier)

The reaction between CaO and SO_2-O_2-SO_3 gas mixtures is relatively slow with a very small temperature coefficient. The apparent rate of reaction is proportional to the area of the CaO-$CaSO_4$ interface. $CaSO_4$, formed in the presence of SO_3, is not protective to CaO, but the coating formed on CaO by SO_2-O_2 mixtures is protective. "Hard burned" CaO reacts readily with SO_3, but only slowly with SO_2-O_2 mixtures.

(2) Desulphurizing of Dilute Gas Streams with MgO (P. Marier)

Finely divided MgO-Fe_2O_3 mixtures were supported on a fiber pad and used at 825°C to remove SO_2 from dilute gas streams. The reaction had an activation energy of about 24 kcal/mole and produced only $MgSO_4$. The efficiency of $MgSO_4$ formation varied with the partial pressure of oxygen in the gas, the ratio of the amount of MgO to fiber, and the linear flow rate of the gases. $MgSO_4$ may be readily decomposed to MgO by decreasing the partial pressure of oxygen in the gas. When the partial pressure was moderately decreased with added CO, concentrated SO_2 was evolved. When an excess of CO was used, COS was evolved. The COS may be converted readily to sulphur by the addition of SO_2 in a second step. The activity of MgO did not decrease with repeated recycling.

(3) The Effect of Time and Temperature on the Kinetics of Formation of NO_x Species (D. MacKinnon)

Nitrogen and oxygen in various proportions were subjected to elevated temperatures and the gaseous products were analysed with a MS 10 mass spectrometer. A maximum in NO formation occurs at temperatures between 3640 and 3680°F and retention times between 6 and 10 seconds. The temperatures at which maximum NO formation occurs is about 200°F lower than that predicted earlier from published thermodynamic and kinetic data. The rate of formation of NO was proportional to the one-half power of the partial pressure of oxygen.

(4) Recovery of Sodium Sulphite from Pulping Operations (R. Kerby)

Sodium sulphite can be recovered from waste sulphite liquors by a process involving pyrolysis of the liquors, followed by solid state carbonation of the smelt and aqueous sulphitation of the resulting sodium carbonate. The rates of carbonation of synthetic smelts were studied in H_2O-CO_2 gas mixtures using pellets and powders prepared from reagent grade Na_2S and Na_2CO_3. The reaction rates were rapid initially, but as it formed, the coating of Na_2CO_3 became increasingly protective to the Na_2S. Maximum rates of reaction were found at temperatures between 125 and 135°C.

PROGRESS IN 1971

The gaseous emission of sulphur dioxide and nitrogen oxide from combustion processes continues to be a major problem in relation to the deterioration of our environment. A number of methods for controlling these emissions are in the development stage, but at present there is no consensus over which method, or set of methods, will eventually offer the best solution to this problem.

One of the more successful dry absorption methods for removing sulphur dioxide from stack gases has been the limestone or dolomite injection process. The process is simple and direct, requires a minimum of investment and uses abundant and low cost reactants. After injection, the limestone or dolomite undergoes calcination at temperatures above 600°C, and the resulting oxides react with sulphur dioxide and oxygen to produce the corresponding sulphates. The calcium sulphate formed is difficult to reduce back to the oxide for recycling purposes, but magnesium sulphate is readily reduced to the oxide.

Kinetic studies were made of the reactions of sulphur dioxide and sulphur trioxide with powdered calcium oxide and fibre-mounted magnesium oxide. Reactions with sulphur dioxide and oxygen were slow and in the case of calcium oxide, resulted in the formation of the intermediate compound, calcium sulphite. Below 650°C, the calcium sulphite oxidized to produce a protective coating of calcium sulphate, while above 650°C, the calcium sulphite underwent a binary peritectoid reaction to form calcium sulphide and calcium sulphate.

Both calcium oxide and magnesium oxide reacted rapidly with sulphur trioxide. After approximately eighty percent conversion, there was a marked decrease in the rate of sulphation. The addition of five weight percent hematite to the calcium oxide powder and the fibre-mounted magnesium oxide,

greatly increased the rate of sulphation in the presence of sulphur dioxide and oxygen, due to the catalytic conversion of sulphur dioxide to sulphur trioxide. The catalytic effect of fly ash, in relation to these reactions, is presently being studied.

The magnesium sulphate formed during the sulphation reaction was reduced at 800°C to magnesium oxide by the use of carbon monoxide. When low flow rates of carbon monoxide were used, concentrated sulphur dioxide was evolved. At higher flow rates of carbon monoxide, carbonyl sulphide was produced. The carbonyl sulphide was reduced to sulphur by the addition of sulphur dioxide over a catalyst in a second step. The activity of the magnesium oxide did not decrease with repeated recycling.

The problem of nitrogen oxide emissions arises whenever nitrogen and oxygen are exposed to temperatures between 3000° and 3800°F. A study was made of the relationship between time, temperature and the rate of formation of nitric oxide. A maximum in nitric oxide formation (14000 ppm) occurred at temperatures between 3640° and 3680°F for retention times between six and ten seconds.

The temperatures at which maximum nitric oxide formation occurred was about 200°F lower than that predicted previously from published thermodynamic and kinetic data. The rate of formation of nitric oxide was found to be proportional to the one-half power of the partial pressure of oxygen and to the first power of the partial pressure of nitrogen. Studies are presently underway to determine what effect carbon dioxide, sulphur dioxide and water vapour have on the rate of nitric oxide formation.

One of the major sources of water pollution in Canada today is the pulp and paper industry. This is particularly true of those pulp mills using the sulphite pulping process, since there is no standard process for recovering the sulphite chemicals from the waste sulphite liquors. One of the processes which is in the development stage involves the pyrolysis of the waste sulphite liquors, followed by solid state carbonation of the smelt and aqueous sulphitation of the resulting sodium carbonate. A study was made of the solid state carbonation of synthetic smelts in H_2O-CO_2 gas mixtures. The smelts were in the form of pellets and powders prepared from reagent grade sodium sulphide and sodium carbonate. Those smelts containing sodium sulphide monohydrate were found to carbonate at a much faster rate than the smelts containing either anhydrous sodium sulphide or a higher hydrate.

The carbonation reaction rates for the smelts containing sodium sulphide monohydrate were rapid initially, but as it formed, the coating of sodium carbonate became increasingly protective to the smelt. The temperature dependence of the reaction rate was complicated, but maximum rates of reaction were found at temperatures between 125° and 135°C. The rate of carbonation was found to be proportional to the carbon dioxide partial pressure, but a more complex relationship was found with respect to the water vapour partial pressure.

RELEVANT PUBLICATIONS

EMA 71-11 Minimizing NO_x Pollutants from Steam Boilers, by D. J. MacKinnon and T. R. Ingraham.

Published thermodynamic and kinetic data were used to show that the formation of nitrogen oxides can be most effectively minimized by distributing the flame front in such a way as to maintain a low temperature-time profile within a boiler.

EMA 71-30 Lime Utilization in SO_2 Scavenging, by P. Marier and T. R. Ingraham.

Increased utilization of lime for SO_2 scavenging can be affected by oxidizing the SO_2 to SO_3 prior to reaction and by increasing the boiler residence time of the lime to the order of three to four minutes.

IC 263 Desulphurizing Gases with MgO - Recovery of Concentrated SO_2 or Elemental Sulphur, by P. Marier and T. R. Ingraham.

Finely divided $MgO-Fe_2O_3$ mixtures were supported on a fibre pad and used at 825°C to remove SO_2 from dilute gas streams. The $MgSO_4$ so formed can be readily decomposed to MgO by the use of CO, with the formation of either SO_2 or COS.

IR 71-14 Residual Nitrogen Oxide at Steam Boiler Temperatures, by D. J. MacKinnon and T. R. Ingraham.

Published data were used in a computer program to predict the change that occurs in the amount of nitrogen oxide (NO) in nitrogen-oxygen mixtures at steam boiler temperatures, when the residence times, temperature and oxygen partial pressure are changed.

IR 71-67 Recycling of Waste Sulphite Liquors for Canadian International Paper Co., Hawkesbury, Ontario, by R.C. Kerby and T.R. Ingraham.

Sodium sulphite can be recovered from waste sulphite liquors by pyrolysis of the liquors, followed by solid state carbonation of the smelt and aqueous sulphitation of the resulting sodium carbonate.

Note on the Mechanism of the Absorption of SO_2 by Limestone, by T.R. Ingraham and P. Marier, APCA Journal, 21 (6), 347 (1971).

Calcium sulfite is formed as an intermediate in the sulfation of calcium oxide with gases containing sulfur dioxide.

Papers

T.R. Ingraham, H.W. Parsons and L.J. Cabri, "Leaching of Pyrrhotite with Hydrochloric Acid", in press, Can. Met. Quarterly.

Paper prepared jointly with the Extraction Metallurgy Division.

Internal Reports

L.J. Cabri and R.G. Pinard, "Separation and Examination of Pyrrhotite Varieties for Hydrometallurgical Testing", Mineral Sciences Division Internal Report MS 71-80, July 1971.

As part of an investigation of acid leaching as an alternative to pyrometallurgical smelting of sulphide ores, samples of monoclinic and of hexagonal pyrrhotite were prepared by magnetic separation from naturally-occurring mixtures. These materials, characterized by optical microscopy, X-ray diffraction, and electron microprobe analysis, were prepared for use in hydrochloric acid leaching experiments done in the Extraction Metallurgy Division.

3.2 - THE MATHEMATICAL MODELLING OF PLUME DISPERSION

by

H. Whaley

- - - -

ABSTRACT

The need to ensure that stack-emitted pollutants from combustion and process sources become sufficiently dispersed in the atmosphere to meet legislated or other air quality requirements led to the development of the CCRL stack-height estimation method. However, it was clear even during the development, that insufficient data on plume behaviour applicable to the Canadian environment was available. This realization led to the CCRL plume dispersion research project which, to date, has collected plume spread data from four sources under widely differing meteorological, climatological and topographical conditions. As the data is accumulated and evaluated it becomes evident that a mathematical diffusion model is required so that accurate predictions of the long and short term effects of plant siting can be assessed.

The CCRL, by using measured data to validate or modify existing dispersion models, is developing criteria by which stack heights can be estimated for effective plume dispersion in any of the main geographic regions of Canada.

INTRODUCTION

The dispersion of a hot gaseous stack-emitted plume containing particulate material is extremely complex with meteorology, climatology, efflux characteristics and particle/gas interactions each having an important influence. A physical model of a plume is usually considered in two discrete stages, namely plume rise and dispersion. In other words the plume is considered to be emitted from a virtual point source origin at the same height as the downwind plume axis. This two stage concept is illustrated schematically in Figure 1, and when accompanied by simplifications of meteorology and topography, facilitates the mathematical treatment.

THE DEVELOPMENT OF PLUME DISPERSION MODELS

The problem of turbulent diffusion in the atmosphere has not yet been uniquely formulated in the sense that a single basic physical model would be capable of explaining all aspects of plume behaviour. Instead there have been two alternate approaches to this problem, one physically based--the gradient-transport theory and the other statistically based--the probability of motion theory. The gradient-transport approach has been used in many scientific areas ranging from heat transfer to electrical theory and depends on the diffusion of material from regions of high concentration to regions of lower concentration. On the other hand the statistical approach, which essentially began with studies of atmospheric turbulence, analyses the motion of fluid elements in the atmosphere and tries to determine the statistical properties necessary to represent diffusion.

The Gradient-Transport Model

The pioneer in the field of gradient-transport diffusion modelling was the German physicist Fick (1) with whose fundamental differential equations most diffusion phenomena can be described. Fickian diffusion principles, or "K Theory" as it is sometimes called has been taken by subsequent workers and solved for different conditions to give variations of the gaussian plume dispersion model.

The Statistical Approach

G. I. Taylor (2) in deriving his fundamental diffusion theorem, laid the groundwork for statistically based diffusion models. In common with "K" theory, this work had considerable influence on all subsequent work in many related areas. Models using the statistical approach may also give rise to the gaussian plume dispersion model.

The Gaussian Model

As mentioned above, the Gaussian diffusion model can be derived either from "K" theory or from the statistical approach. Strictly speaking the model only applies for a long diffusion time and for the homogeneous stationary conditions necessary to "K" theory. However, it has been argued that the gaussian function distribution may provide a general description of plume diffusion because of its essentially random nature and the analogy with the central limit theorem of statistics. Examples of the use of "K" or statistical theory to derive gaussian plume models are to be found in Pasquill (3), Sutton (4), and Bosanquet (5).

The CCRL Model

It was evident that when the CCRL began its plume dispersion research project that a suitable model might be the well-substantiated and accepted gaussian diffusion model. It was also clear that the Pasquill model as modified by Gifford (6) was generally the most suitable.

In this variation of the model, the spreading gases are distributed across the plume in the directions perpendicular to the mean wind flow according to the normal or gaussian distribution function. One of the main virtues of this distribution is that it is completely defined by its standard deviation. This means that horizontal or vertical spread parameters obtained for real plumes must necessarily be, or be related to the standard deviation of their respective concentration profiles. This standard deviation, however, is obtained solely from the measured data, and is not dependent on the type of model used except that it must appear either directly or indirectly as a term in the mathematical formulae.

As more data on plume spread is acquired it becomes evident that the long-term average gaussian diffusion model does not describe the measured data in some instances. This is especially so close to the stack where the diffusion time is short, such that the measurements cannot be considered to represent an average condition. The main departure from the gaussian model is that the infinite fringes predicted by the model are seldom found. In fact it is clear that diffusion is greater at the plume fringes and much less on the axis than a gaussian model would predict. A re-examination of "K" theory suggests an explanation to this phenomenon. Small atmospheric eddies acting on the fringes are in a region of maximum concentration gradient and therefore provide an effective dispersing mechanism, whereas those at the peak are in a region of zero gradient and are therefore not as effective. Preliminary studies indicate a slight modification to "K" theory in which the eddy diffusivity is not held constant but varies according to its position with respect to the plume axis. This incorporates an extra degree of freedom in allowing the plume boundary to be specified from the measured data. Figure 2 shows an example of a plume profile in which the normal curve provides a good description. Figure 3 has been chosen to illustrate the serious discrepancy which can arise in some instances. It can be seen that the normal curve over-estimates the peak and edges. The distribution modification is also shown and provides a better description of the measured data, especially after averaging about the plume centreline.

CONCLUSIONS

When sufficient measured plume dispersion data becomes available it will be possible to validate a mathematical model based on both physical and statistical fundamentals. It will then become possible to apply more reliable dispersion estimates in the following important areas.

(a) Stack height estimations, to avoid excessive or objectionable pollutant levels at receptor locations.

(b) Plant siting problems, which may be resolved in relation to the surrounding community.

(c) Dust or pollutant removal equipment design.

(d) Assess the effect of growing industrialisation on the delicate environmental balance of the Arctic.

REFERENCES

(1) Fick, A. Über Diffusion, Ann. Physik. Chem. 2 94: 59-86, 1855.

(2) Taylor, G.I. Diffusion by Continuous Movements, Proc. London Math. Soc. 2 20: 196-202, 1921.

(3) Pasquill, F. The Estimation of the Dispersion of Windborne Material, Met. Mag. London 90 33-49, 1961.

(4) Sutton, O.G. The Dispersion of Hot Gases in the Atmosphere, J. Met. 7 307-312, 1950.

(5) Bosanquet, C.H. and Pearson, J.L. The Spread of Smoke and Gases from Chimneys, Trans. Farad. Soc. 32, 1249-1264, 1936.

(6) Gifford, F.A. Jr. Uses of Routine Meteorological Observations for Estimating Atmospheric Dispersion, Nuclear Safety 2, 4: 47-51, 1961.

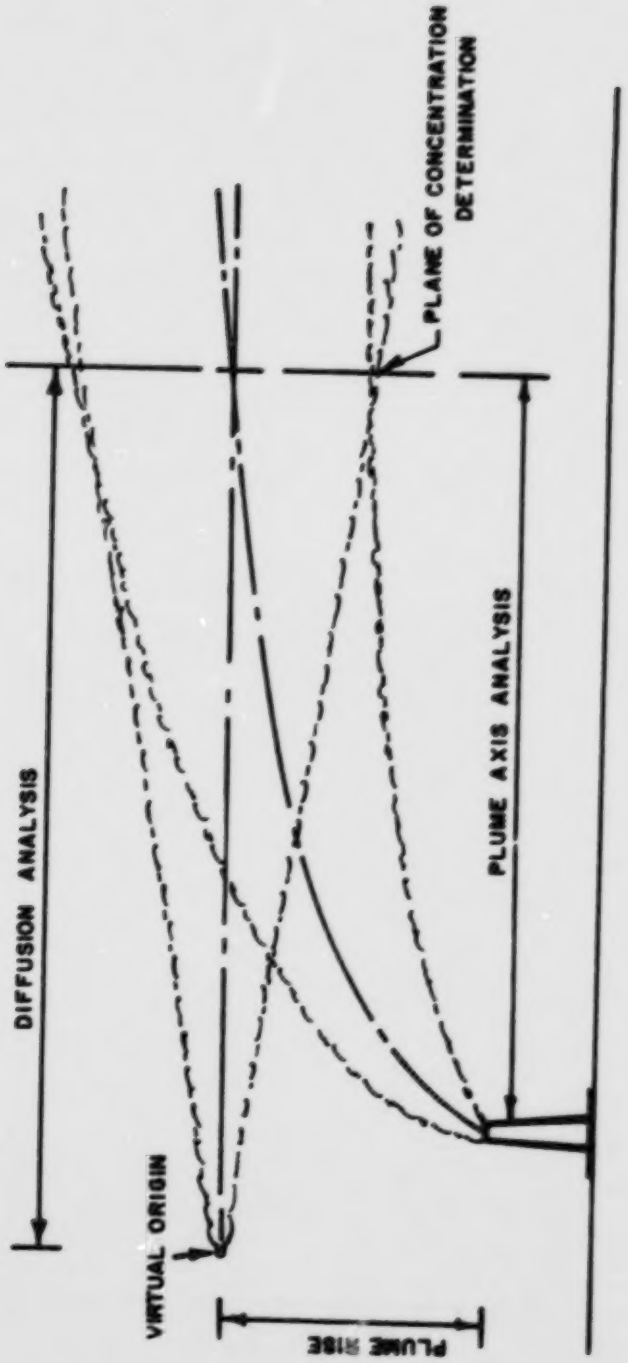


Figure 1. A typical two-stage plume dispersion model.

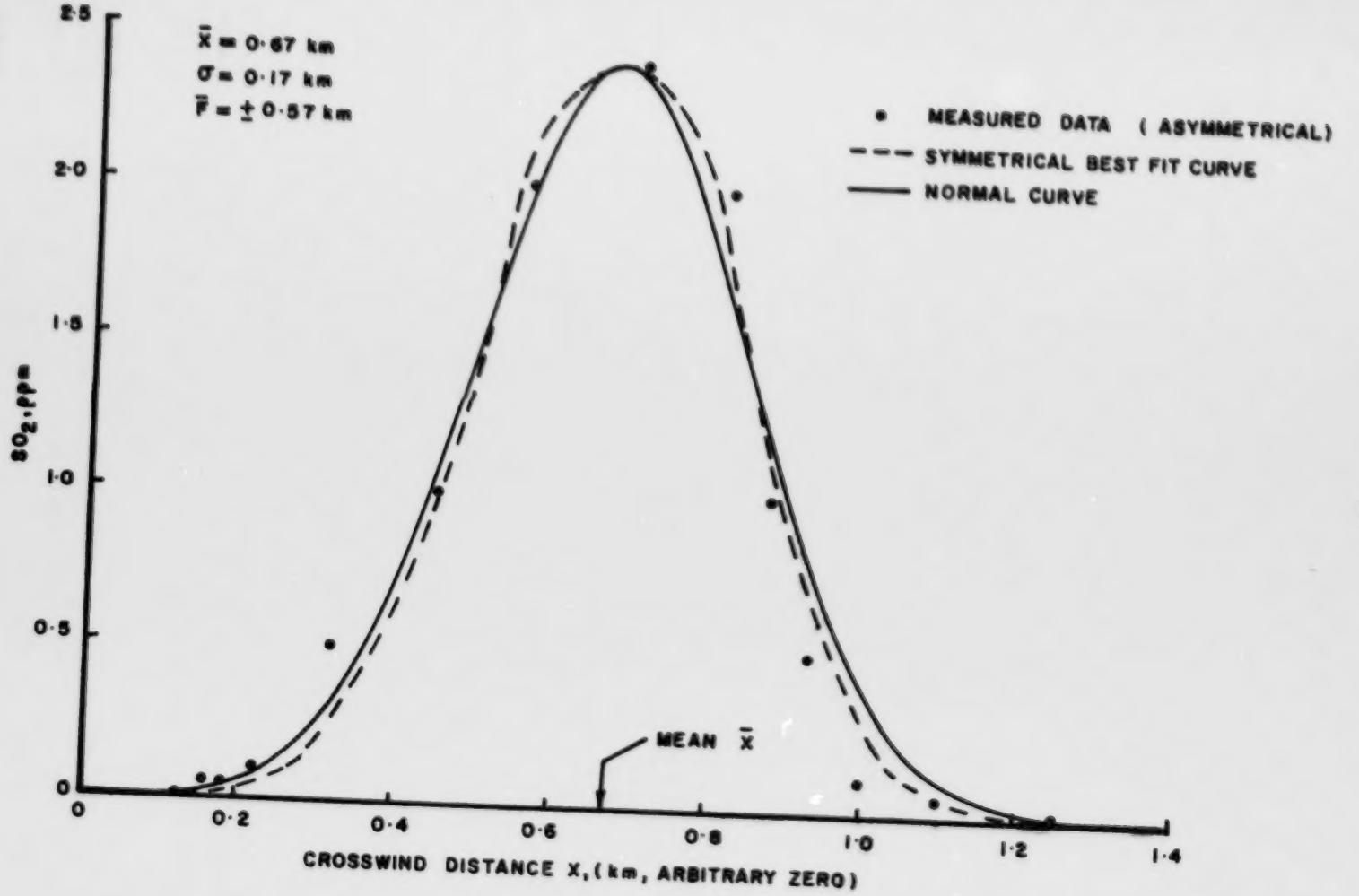


Figure 2. Example of a near-gaussian horizontal crosswind SO_2 profile.

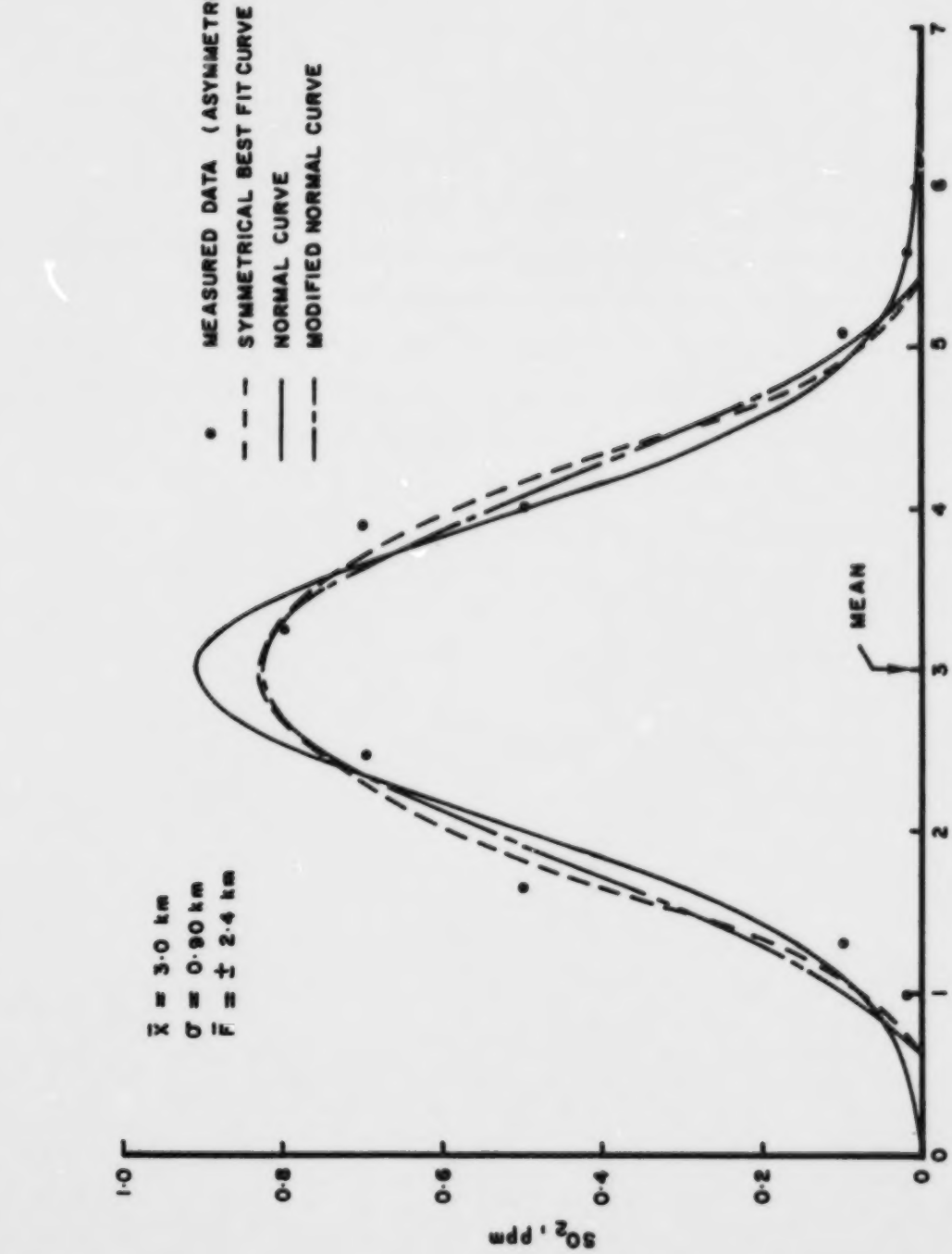


Figure 3. Example of a non-gaussian horizontal crosswind SO_2 profile.

3.3.1 - ANALYSIS OF SULPHUR IN OIL AND COAL BY X-RAY FLUORESCENCE TECHNIQUES

by

D.S. Montgomery

ABSTRACT

The Mines Branch has been interested in the development of a rapid portable method of determining sulphur present in petroleum and coal particularly lignite as many samples have to be analysed in the forthcoming resource evaluation program. A Pananalyzer X-ray absorption apparatus has been tested on a wide variety of petroleum fractions having a wide range of sulphur contents. The results on oils indicate that comparable accuracy with the ASTM bomb method can be achieved unless sodium chloride is present as is the case in certain crude oils. The results obtained so far on coals shows that considerable improvements have to be made to reduce the interference of other elements.

3.3.2. - THE CARLE THERMAL ANALYSIS SYSTEM FOR THE DETECTION OF TRACE QUANTITIES OF HYDROCARBONS

by

M. L. Boyd

In connection with the present research program of characterizing low grade oils (especially the heavy ends) by physical methods (in particular, their thermal properties), an instrument has been acquired which could be potentially useful in environmental studies. This is the Carle Model 3000 Thermal Analysis system. In this instrument the sample is pyrolyzed under controlled atmospheric conditions directly into a special high temperature flame ionization detector which acts as a mass detector of organic carbon. This permits rapid quantitative determination of organic carbon in extremely small quantities, such as trace organics collected on air filters. Rates of organic carbon evolution as low as 0.01 μg per minute can be detected. A special vapour pressure probe and accurately known very low nitrogen flow rates permit the determination of continuous vapour pressure curves as low as 0.1 millitorr. This could be useful in environmental studies related to toxic organic chemicals. Another unique property of this instrument is the insensitivity of the flame ionization detector to water. This provides a technique for the analysis of trace organic contaminants (in parts per billion) in water. The volatility pattern of the trace organic can be associated with the source of the contaminant. This latter application could be particularly useful in studying oil spills.

3.3.3 - INVESTIGATION OF SULPHUR COMPOUNDS IN LOW GRADE CRUDE OILS

by

Henry Sawatzky

ABSTRACT

The sulphur compounds in low grade crude oils with high sulphur contents are being studied in order to gain a better understanding of them for desulphurization and for the possible utilization of them. Also, a method is being developed for the use of the sulphur compounds for the identification of sources of oil spills.

The study of these sulphur compounds is being made by gas chromatography using specific sulphur detectors. The conventional gas chromatographic column packings that are able to separate petroleum fractions according to types are thermally unstable and therefore completely inorganic thermally stable column packings have been investigated with considerable success. These new packings have been used to separate distillate fractions into numerous cuts of concentrated sulphur compounds.

An analytical desulphurization technique has been developed for the purpose of characterizing micro quantities of sulphur compounds that are separated by gas chromatography.

PROGRESS IN 1971

Since sulphur in fuels is the cause of major pollution, a study is being made of the sulphur compounds in low grade oils. A better understanding of the structures incorporating the sulphur might lead to better methods of sulphur removal. Perhaps some of these sulphur compounds could be utilized and markets found for them. We are also involved in an investigation of the possibility of using these sulphur compounds for identification of sources of oil spillages. There are many sulphur compounds in petroleum that would not be readily lost by evaporation, oxidation, or bacterial degradation and thus should be ideal for identification purposes. This project is financially supported by Inland Waters.

The gasoline and kerosine fractions of some crude oils have been investigated fairly thoroughly in other laboratories, but the heavier fractions that contain most of the sulphur have received little attention. We are attempting to investigate as much of the heavier material as possible by gas chromatography because this allows us to use specific sulphur detectors, avoid dilution by solvents, and provide very efficient separations. Fractions distilling over narrow temperature ranges are separated by gas chromatography into numerous cuts of sulphur concentrates as well as non-sulphur materials. Unfortunately, the conventional column packing materials required for these separations contain polar organic liquids that are thermally unstable and thus contaminate the separated products from heavy petroleum fractions. For this reason, we have become interested in thermally stable inorganic column packings.

During the past year, we have made an intensive investigation of inorganic materials that might be used for column packings and have had considerable success. The most suitable material found so far is lithium chloride coated

acid washed diatomaceous earth. The acid washing which removes the aluminum and iron oxides from the diatomaceous earth results in reduction of the retaining power, thereby lowering the required operating temperature. Also, the efficiency of separation is vastly improved. The diatomaceous earth by itself can cause a certain amount of separation, but coating it with the lithium chloride increases the resolving power by an order of magnitude in some cases. A number of Athabasca bitumen fractions have been separated on this salt-containing column packing. About one-quarter of the sulphur in the unseparated material could not be accounted for after separation. These are believed to be dialkyl sulphides because from our work with pure compounds it has become clear that these sulphides would be retained on the packing. Also, we have found no evidence for them during mass spectroscopy of the separated cuts. Thus it is clear that backflushing of the chromatographic column will be required to recover the alkyl sulphides. All other types of sulphur compounds, even those containing two sulphur atoms, are not excessively retained. The same applies to polynuclear aromatic hydrocarbons with large clusters such as pyrene. These inorganic columns deteriorate with use and have to be frequently regenerated by passing oxygen through them at elevated temperatures.

We have found that bitumen with a boiling temperature corresponding to over 350°C at atmospheric pressure cannot be distilled efficiently under vacuum at temperatures low enough to avoid thermal degradation. Therefore, we have modified a gas chromatographic simulated distillation by technique so that it can be used to collect fractions. In this technique, non-polar thermally stable silicone rubbers are used in column packings. With this technique we are able to separate bitumen with a boiling range up to 550°C, according to boiling point, at temperatures below 300°C. This separation is much more efficient than conventional distillation, but the disadvantage is the small amount of material that can be handled. However we require only small quantities.

In order to help identify the sulphur compounds that have been separated from the bitumen, we have modified an analytical desulphurization technique that was developed by the U. S. Bureau of Mines. We have reduced the minimum

amount of material required to less than 1/20 of the amount claimed possible by the unmodified technique. This involved desorption from the catalyst that was apparently not required in the unmodified method. The desulphurized products are lower in molecular weight than the hydrocarbon accompanying the sulphur compounds in the sulphur concentrated cuts and thus can be characterized.

As far as the oils that are being studied are concerned, we have so far done most of our work on Athabasca bitumen. However we have acquired other Canadian crudes for this work that are being produced in substantial quantities and might be of geochemical interest. We have included Alaskan Prudhoe Bay oil in order to find out whether it can be identified from other oils.

PAPERS AND REPORTS OF 1971

Gas Chromatographic Separation of Sulphur Compounds from Athabasca Bitumen, by H. Sawatzky, G. T. Smiley, A. E. George and D. M. Clugston, ACS Div. Fuel Chem., Preprints 15, 83 (1971). (Presented at the ACS Meeting in Los Angeles, March 1971).

Divisional Reports - limited circulation

Evaluation of Some Inorganic Column Packings for Gas Chromatographic Separation of Petroleum Sulphur Compounds, by A. E. George and H. Sawatzky, FRC 71/19-RBS.

Identification of Sources of Oil Spills, by A. E. George, D. S. Montgomery and H. Sawatzky, FRC 71/29-RBS.

Ulta Microhydrodesulphurization Technique for the Characterization of Petroleum Sulphur Compounds, by H. Sawatzky and G. T. Smiley, FRC 71/69-RBS.

Gas Chromatography and Mass Spectroscopy of a High Boiling Point Bitumen Fraction Involving Column Packings with Lithium Chloride, by H. Sawatzky, G. T. Smiley and D. M. Clugston, FRC 71/72-RBS

Evaluation of Lithium Chloride-Diatomaceous Silica Systems for Gas Chromatography of Petroleum Sulphur Compounds, by A. E. George, G. T. Smiley, and H. Sawatzky, FRC 72/6-RBS.

3.3.4 DEVELOPMENT OF METHODS FOR DETERMINING SULPHUR, HEAVY METALS OIL AND WATER IN COALS AND COAL PRODUCTS

by

B.J.P. Whalley*, S.M. Ahmed** and W.R. Leeder***

ABSTRACT

In this period, a volumetric titration of sulphate ion by barium perchlorate using Arsenazo (III) has been shown to be successful as a volumetric finish to the Eschka (ASTM) method for total sulphur in coal. The procedure is easy, rapid and evidently more precise than the gravimetric finish at low (< 0.5% S) sulphur values.

The method has also been shown to be easier than the barium perchlorate/Thorin titrimetric method for trace amounts of sulphate ion in relatively pure water.

Investigation of electron spectroscopy for determinations of organic sulphur in coal and the Dithizone colorimetric method of mercury analysis in coal and coke-oven by-products was initiated.

It has been shown that reliable determinations of small amounts of oil in oil-dewatered coal fines by extraction methods is markedly affected by the coal rank and evidently by the penetration of oil into the coal structure.

---

*Head, **Scientific Officer and ***Research Scientist, Special Studies Group, Metals Reduction and Energy Centre, Dept. of Energy, Mines & Resources, Ottawa.

PROGRESS IN 1971

3.3.4.1 Titrimetric Methods of Sulphur Analysis

A number of titrimetric analytical procedures for total sulphur in coal and for sulphate ion in water under development at the Metals Reduction and Energy Centre are directly applicable to problems in analysis of sulphur compounds connected with studies of pollution by airborne and waterborne sulphur oxides. The procedures are based on the use of barium perchlorate as titrant for sulphate ions and Arsenazo (III) [1] [2]. In this period the titrimetric procedure was also been applied to the Eschka method for total sulphur analysis of coal [3]. The elapsed time for a single determination by the ASTM procedure is preferably about 20 hours (overnight) but can be reduced to 10 hours. By substituting the titrimetric for the gravimetric finish, the elapsed time is reduced to about 4 hours.

The proposed Eschka modified procedure is to titrate the Eschka-mixture solution after first removing the cations (especially the high concentration of magnesium and sodium ions) by ion exchange.

Besides reducing the elapsed time for a determination, the titrimetric finish is more easily used by less experienced analysts and evidently provides more precise analyses at lower (< 0.5%) sulphur levels than the standard Eschka procedure.

The titrimetric procedure has also been applied to analysis of practically pure water containing trace amounts of sulphate ion. After removal of cations, titration is made paying particular attention to the pH of the iso-propanol/water medium. Titrations with good precision were obtained at the 5 ppm level of sulphate concentration [4].

Besides cation interference, the accuracy of titration is also reduced by anion interference. Investigation is in progress of the quantitative effect of interference of those anions commonly associated with natural waters and those expected to be associated with common industrial stack-gas scrubbers. Such anions include: phosphates, nitrate, chloride and fluoride.

3.3.4.2 Electron Spectrographic Method for Organic Sulphur Analysis of Coal

There is presently no method of determining organic sulphur in coal directly; its chemical determination by difference (i.e. total sulphur less inorganic sulphur) is of questionable reliability. Application of electron

spectroscopy to the analysis of the different forms of sulphur is therefore being explored. Electron spectroscopy for chemical analysis (ESCA) is a technique which can distinguish the various oxidation states of most of the elements in the periodic table. This is a particularly good technique for the low molecular weight elements which are often difficult to analyse spectroscopically. This program is being carried out in co-operation with Dr. D.C. Frost of the University of British Columbia (U.B.C)[5]. Results of three preliminary lots of analyses are interesting but are inconclusive. However, an equipment improvement in the spectrometer at U.B.C. is expected to give a clearer indication of the possibilities of this approach.

Besides distinguishing between organic and inorganic sulphur (principally pyrite) it is hoped that the method will follow changes in the sulphur distribution between organic and inorganic phases during coal carbonization.

3.3.4.3 Analysis of Coals, Coke-Oven By-Products and Coal Processing Effluents for Heavy Metals

Mercury: Development of Analytical Methods

Analysis of coals for mercury has been resumed in this period. On the basis of a literature review of methods of mercury analysis in coal[6], the Dithizone colorimetric approach has been chosen as appearing to be as accurate as any of the readily available methods as well as requiring only simple equipment. However, a high degree of technical skill and chemical knowledge is required to prevent significant loss of mercury in the sample (a problem peculiar to mercury analysis) and to prevent trace contamination to samples and reagents. The establishment of procedures by the use of standard samples is presently in progress with already promising precision in the 0.1 mg/ml (ppm) range.

Procedures for concentrating and extracting mercury for analysis are expected to be undertaken soon.

3.3.4.4 Evaluation of Analytical Methods for Determining Water and Oil Content in Oil-Dewatered Coal Fines

A serious source of air pollution in coal washeries results from fluid-bed drying of fine (-0.5 mm) coal. With an increased proportion of these fines resulting from mechanical mining and the mining of the unusually

friable coals typical of Western Canadian coal fields, alternative methods to fluid-bed drying are being sought. One alternative approach is to use mechanical de-watering, especially in centrifuges, in the presence of oils or tars. This approach has been investigated in a laboratory and on a pilot scale by the MREC laboratories (7) (8) and is being tested in a commercial coal washery in Western Canada (9).

One of the problems associated with this approach is to find a reliable method of determining the water and oil content of the oiled coal. A survey of instrumental methods was made (10). Experimental evaluation of current analytical methods indicates that the water determinations by a modified Dean and Stark method are generally reliable but that at the lower levels of oil content (2% oil) oil determinations may be unreliable unless knowledge of the coal and history of oiled samples is taken into account. This is probably because oils can be strongly adsorbed in the internal structure of coals, especially of lower rank, and the oil can be subsequently difficult to recover analytically.

Evaluation studies are not yet complete.

REFERENCES

1. Ahmed, S.M. and Whalley, B.J.P. (1969), "The Use of Arsenazo (III) in the Determination of Total Sulphur in Coal by the Oxygen-Flask Method", Fuel (Lond.) 48, 217-219.

2. Ahmed, S.M. and Whalley, B.J.P. (1971), "Anaysis of Total Sulphur in Canadian Coals by a Modified Oxygen-Flask Method Using Aresenazo (III)", Fuel (Lond.) in press, Divisional Report MREC 71/79 (1971).

3. Ahmed, S.M. and Whalley, B.J.P. (1972), "A Volumetric Finish for Eschka Analysis Using Arsenazo (III)", Division Report MREC 72/10.

4. Ahmed, S.M. and Whalley, B.J.P. (1971), "Titrimetric Determination of Trace Amounts of Sulphate Ion Using Arsenazo (III)", Divisional Report MREC 71/108, Submitted to Analytical Chemistry.

5. Leeder, W.R. and Frost, D.C. (1972), "ESCA Determination of Forms of Sulphur in Coal" (pending).

6. Ahmed, S.M. and Whalley, B.J.P. (1970), "Analysis for Mercury in Coals" Part 1. Review of Current Methods", Divisional Report MREC 70/59.

7. Whalley, B.J.P. and Ahmed, S.M. (1967), "Improved Centrifugal Dewatering of Fine Coal by Means of Oil Additions", Divisional Report FD67/101 - MET.

8. Visman, J., (1971), "Coal Washery Design - 1 The E.M.R. Process" Mines Branch Technical Bulletin TB 141 September 1971.

9. Visman, J., Rozenhart, C.F.J., van Cruyningen, J.P., Walsh, J.H., and Whalley, B.J.P. (1971), Can. Pat. 876,860 July 1971, "Process and Apparatus for Separating and Dewatering Coal and Other Minerals".

10. Leeder, W.R. (1971), "Moisture Determination in Coal by Instrumental and Non-Routine Methods", Divisional Report MREC 71/77.

11. Leeder, W.R. (1972), "Utilization of Discarded Automobile Tires in Coking Processes" (pending).

3.4 - MINE AIR QUALITY-DUST AND RADIATION

by

T.S. Cochrane

ABSTRACT

The prime research objective of the Environmental Control Program of the Mining Research Centre is to improve the quality of mine air through understanding and assessment of the physical nature of the respirable hazards.

The dust and radiation project is divided into basic and applied categories. The basic studies are concerned with the development and design of new dust and radiation measuring instrumentation and survey techniques. The applied studies are undertaken in cooperation with other research agencies, mining companies, or governmental departments, to solve or alleviate existing problems.

During 1971, four studies, two basic and two applied, were advanced by four full-time and eight part-time professionals at a cost estimate of $100,000. The progress made is detailed in ten reports, four of which were presented to international, national and local audiences. One major summary report was completed in internal format.

PROGRESS IN 1971

The laboratory study comparing a wide range of dust sampling instruments in pure mineral dust clouds was brought to a close this year with the issuance of an internal report (MR 71/119). This report is being upgraded to Research Report status for wider distribution.

The first stage of the field testing of dust measuring instruments for use in metal mines begun in 1970 in cooperation with the McIntyre Research Foundation and the Mines Accident Prevention Association of Ontario, was completed early in 1971 and four internal reports have been prepared under the general title, "Testing of Dust Sampling Instruments for use in Ontario Mines", parts I to IV. The conclusions of this phase of the study were:

1. there was very poor correlation between the types of instrument examined;

2. size selecting gravimetric samplers can be used in metal mines;

3. in mines with more than 10% quartz in the ore, X-ray diffraction estimation of quartz on the samples collected by the gravimetric samplers gives, in many cases, a better estimate of the health hazard and is more sensitive than weighing;

4. The composition of the airborne dust is very variable, in mines using diesel-powered equipment large quantities of 'combustible' dust, up to 3 mg/m^3, have been found in the general body of mine air;

5. personal samplers indicate that in some operations, miners may be exposed to a 50% higher dust concentration than that in the general body of air in the working place.

The second stage of the study concerned with the problems involved in using personal size-selecting, self-contained dust samplers is underway.

The laboratory study into X-ray diffraction analysis of quartz directly on dust samples collected by small, self-contained, size-selecting gravimetric dust samplers has continued throughout the year. A paper on the calibration and technique was presented at the American Industrial Hygiene Conference in May. During the year, all the samples collected for the cooperative program described above have been analysed for quartz. It has been found that quantities of quartz down to 0.02 mg/m^3 or less can be detected; this is one-fifth of the recommended threshold limit value. The measurement is subject to interference (by other minerals); however, to date it has been found that at least one of the three strong quartz lines (1,0,0) (1,0,1) and (1,1,2) can be used for quartz estimation on all the samples taken underground and in the laboratory. The limiting factor in sensitivity for quartz is interferences rather than counting. Towards the end of the year, work was started on quantitative estimation of other minerals, as this is required in the project "Dust from Canadian Rocks".

In the study on dust from Canadian rocks, the relationships between the airborne dust and the rock properties are being determined using a laboratory set-up. Three ores have been tested so far and the results obtained are being analysed.

The project on filtering mine air undertaken in cooperation with Denison Mines Ltd., has been terminated. The results are presented in two reports, "Mechanical filtration of aerosols in trackless uraniun mine: II - final summary" and "The use of vermiculite to control dust and radon daughters in underground uranium mine air". The conclusions reached through this study are:

1. relatively low efficiency filters - 30 - 40% - for radon daughters and respirable dust may be very useful in meeting approved conditions in sections of the uranium

mines where conditions are near the threshold limit values;

2. high efficiency filters clog rapidly in some cases, and are very expensive. They require pre-filters for a reasonably long useful life;

3. vermiculite is a suitable material for constructing filter beds because of its low cost and low density. Four to eight-inch thick beds for 200 to 500 ft/min face velocity appears optimum;

4. passage of the air through a large room at low velocity may be a practical method of removing larger particles above respirable size by settling (compare horizontal elutriator principle). Such a process can be as effective as some pre-filters;

5. for small volumes of very clean air in a limited space, a good pre-filter and high efficiency main filter in combination can be used.

In the project, calibration of laboratory and field radiation measuring equipment, progress has been made in the year. It has been found that the gamma radiation background is high throughout the area and that a massive lead shield has to be used to shield the radiation detector in many of the calibrations. A report entitled "Preliminary measurements of gamma ray background in the Elliot Lake area", by R. A. Washington and H. Montone is being prepared.

Two field instruments for alpha particle (radon daughter) assessment have been tested in the laboratory and underground during the year. One, designed by the Health and Safety Laboratory of the U.S. Atomic Energy Authority appears very suitable for mine use, although it is a little heavy and somewhat expensive. The second unit (Victoreen Thyac III) is less suitable because of its shorter time constant and consequently larger meter fluctuations. Field tests of these and other similar instruments are continuing.

Work is in progress on testing a wide range of filter materials to see if a more suitable compromise between radon daughter collection and alpha particle assessment can be developed. The sampling pumps at present in use are heavy and the sensitivity of the whole system is not adequate for the proposed standard of 0.3 working level.

Other techniques for assessing radiation exposure in mines are also being examined. Two studies in the preliminary stages are: thermoluminescent chips, and an electronic solid state alpha particle detector.

BIBLIOGRAPHY

1. Knight, G. and Kowalchuk, R., "Testing of Respirable Dust Sampling Techniques for use in Ontario Mines: Part I. Description of Techniques", MR 71/16 - ID.

2. Knight, G., "Testing of Respirable Dust Sampling Techniques for Use in Ontario Mines: Part II. Elliot Lake Detailed Dust Measurements", MR 71/44 - ID.

3. Knight, G. "Comparison of Angle and Energy Resolution System in Quatitative X-Ray Diffraction Analysis of Quartz in Airborne Dust Samples", MR 71/70 - ID.

4. Washington, R.A., "Survey of Radiation Leaks from the X-Ray Diffraction Apparatus in the Elliot Lake Laboratory", MR 71/90 - ID.

5. Knight, G., "Comparison of Dust Sampling Instruments", 71/119 - ID.

6. Windish, J., et al, "Dust Survey No. 26 Colliery of Cape Breton Development Corporation (Coal Division) Glace Bay, Nova Scotia", Dept. of National Health and Welfare (February 1971), 71/1.

7. Cochrane, T.S., "Routine Dust Measurements and Standards", Pres. at AGM CIMM Quebec City, April 27, 1971, MR 71/28 - ID.

8. Knight, G., Stefanich, W. and Ireland, G., "Laboratory Calibration of a Technique for Determination of Respirable Quartz MR 71/33 - LD.

9. Washington, R.A., and Montone H., "Preliminary Measurement of Gamma Ray Background in the Elliot Lake Area", in editing process.

10. Washington, R.A., et al, "Mechanical Filtration of Aerosoles in Trackless Uranium Mine - Part 2 - Final Summary" edited and now being numbered.

11. Washington, R.A., et al, "The Use of Vermiculite to control Dust and Radon Daughters in Underground Uranium Mine Air", in final draft.

3.5 - SUMMARY OF DIESEL INVESTIGATION FACILITY PROGRESS DURING 1971

by

E.D. Dainty and J.P. Mogan

INTRODUCTION

The Canadian Explosive Atmospheres Laboratory (CEAL) Diesel Investigation Facility was established to ensure the control of exhaust emissions from diesel-powered mining equipment and safety with regard to explosion hazards. The design stages of this laboratory were completed in January of 1970 and the official end of the construction stage was November of 1971. It is expected that final installation of remaining instrumentation will be completed by May 1972.

PREPARATORY STAGES

Before the laboratory could be made 100% operational it has been necessary to perform various preliminary studies which include:

1. explosion bunker leakage tests to avoid destruction due to gaseous detonation in circulation ducts,
2. explosion bunker explosion tests to ensure personnel safety,
3. engine control and readout systems checkout tests, and
4. dynamometer systems start-up tests.

Items 1, 2 and 4 have been completed and some instrumentation associated with item 3 remains to be installed and assessed.

EMISSION ANALYSIS EQUIPMENT CHECKOUT

The heart of the Laboratory's ventilation research and Diesel certification work is the Beckman Analyzer Cart. There are five infra-red analyzers built into the cart: low CO (having 3 ranges - 0 to 1000 ppm, 0 to 2000 ppm and 0 to 5000 ppm), high CO (2 ranges - 0 to 1.5 percent and 0 to 7.5 percent), CO_2 (2 ranges - 0 to 5% and 0 to 15%), CH_4 (methane 2 ranges - 0 to 2% and 0 to 10%), and finally NO (or nitric oxide in 3 ranges - 0 to 500 ppm, 0 to 2000 ppm and 0 to 4000 ppm). In addition there is a para-magnetic oxygen analyzer incorporated. The ranges chosen are broad enough to permit analysis of the exhaust of normal internal combustion engines within a resolution of 1% of full-scale. The outputs from the analyzers are directed to linearizers which condition the signal so that the chart on the 8-point recorder can be read directly. The output meters on the analyzers can also be read and output converted to percentage by means of the calibration curves.

Start up of this apparatus was completed in January of 1972. Experimental verification of the manufacturer's calibration curve characteristics has been completed for all gases with the exception of O_2 and NO. This has been accomplished with the aid of a CEAL developed "Gaseous Mixture Preparation Apparatus" which affords precise and easy dilution of a known mixture, thus permitting a detailed check of each analyzing instrument throughout its complete range.

It is interesting to note that a difficulty with NO analysis arose due to the release of plasticizer from the surface of the 5/16 inch polyethylene tubing. This took place in sufficient quantities to contribute to a background response necessitating a check on the results for this gas. Quarter inch tubing ordered at the same time did not exhibit this same undesirable characteristic.

EMISSION VOLUME MEASUREMENT

In order to specify the ventilation requirements for a given machine, the exhaust quantity must be known in addition to its analysis. A selection of venturi tubes has been purchased to measure aspirated air corresponding to outputs of up to 400 BHP. These will be calibrated against primary standards and will provide better than one percent accuracy at full scale.

CERTIFICATION ACTIVITY

Several conferences with some provincial authorities and equipment manufacturers and a concerned mining association, have already taken place in order to better acquaint the interested parties with the available services of the laboratory.

Three vehicles have recently been certified by this Laboratory. The first was a type 60ED31 Torkar Shuttle car incorporating an indirect injection type Caterpillar Model D333C-NA engine (146 BHP @ 2200 RPM) which required 17000 cfm of ventilating air per vehicle in accordance with bulk air concentrations specified in Schedule 30 of the United States Bureau of Mines.

The second and third vehicles were Kaiser CJ5 personnel carriers each incorporating a direct injection Perkins Model 4.236 engine (65 BHP @ 1700 RPM) which required 17,100 cfm of ventilating air per vehicle according to the same standard.

The superiority of the indirect injection engine is made evident from a ventilation point of view by comparison of the above figures. This is one reason why the Deutz air-cooled engines of the indirect injection type have found such a large market underground in Canada.

In this country, the ventilation aspect of mine operation assumes greater importance than in warmer climates because often there is a necessity to heat large quantities of air before passing it into the mines. Indeed, one of the provincial regulation agencies has suggested that investigation of possible ventilation reduction in view of this economic penalty could be a valuable research project. Furthermore, present rules of thumb have proven to be either penalizing economically or inadequate from a health point of view. Thus assessment of load factors, type and location of service, careful engine selection, among other factors, becomes very important, particularly in Canada. Consequently, it is desirable that the safety margins inherent in ventilation requirements such as those proposed by the United States Bureau of Mines, be carefully evaluated to see where and how they can be improved to better accomodate Canada's particular circumstances.

In this connection, the Diesel Laboratory has laid the ground work for nine research studies.

RESEARCH PROGRAMME

The following research subjects have arisen through consultation with provincial government officers, the Ontario Mining Association, vehicle and engine manufacturing firms, and the Mining Research Centre of this Branch.

1. Continuous Monitoring of Vehicle Environment

Normal ventilation practice calls for monitoring the bulk mine air in the return air ways. This prevents the average air concentrations of toxic constituents from becoming excessive. It does not however prevent concentrations in local areas from becoming excessive such as at an ore face where ventilation flow is not well defined nor easily controlled.

Thus there results a real concern expressed by the Ontario Mining Association that rugged continuous monitoring equipment be installed on units in vicinities which are difficult to ventilate, and that this practice should become the norm. This is particularly important when it is considered that high powered diesel drilling equipment (200 BHP) is proposed by a prominent equipment supplier in Canada, thus substantially increasing the potential toxic emissions risk.

Several CEAL personnel have become familiar with gas detection and alarm systems as a result of investigating some fifteen such detection systems. The present state of the art appears to economically prohibit individual monitors to protect the driver of each machine but efforts will be made to pay considerable attention to this important aspect.

2. Exhaust Dilution

One way of reducing the local hazard is to effectively dissipate the exhaust into the surrounding air bulk. Sometimes this is done by directing the exhaust into the cooling fan. Recently, manufacturers have marketed venturi pump devices which use the exhaust to entrain air quantities of up to 20 times the exhaust volume. A Provincial Authority expressed a desire to have an independent confirmation of the efficient performance of these devices throughout the load-speed range of engine operation. The Diesel facility is admirably equipped to perform such a study and this likewise will be undertaken in due course.

3. Exhaust Recirculation

As stated above higher horsepower vehicles are anticipated for use in areas where confinement makes exhaust dissipation difficult. Thus, the effects of recirculation of exhaust into the air intake become of greater interest because of the consequent deterioration of the quality of the exhaust emissions. This diesel facility will be easily adapted to perform such studies.

4. Load Factor

Little data is available on the subject of operating output level of underground machinery and the time period at that output level. This matter bears directly upon the ventilation margin because the toxic emissions vary greatly with loading. Therefore, this Diesel Laboratory is co-operating with an engine manufacturer and a large mining concern to instrument vehicle(s) to better establish this factor and reduce the ignorance associated with the operating mode of various machinery types. This necessitates the acquisition of in situ measuring techniques and equipment for the several variables of load or torque, fuel consumption and speed.

5. The Effects of Engine Wear

A further aspect of the load factor study is a study of the nature of exhaust quality deterioration with engine wear. Certification ventilation is usually based on the full load, full speed performance of a new engine. On the other hand maintenance and overhaul requirements are often dictated by a large increase of CO in the exhaust which is usually the result of engine use. Normally one could say that a practical load factor of less than full load would compensate for this increase in CO with wear. The picture is clouded however, because almost always, the ventilation is governed by the production of NO_x. As a rule, as CO increases with wear, NO_x decreases. Thus it could easily be that up to a certain point wear is beneficial and the ventilation requirements could very well be reduced. A project which will require up to two years of field and laboratory tests is now in process to sort out the economic possibilities in this area.

6. Several Additional Studies

Further studies which need not be described in detail but which relate to the above studies or are designed to assist mine managements and the inspectorates to perform their functions more effectively are the·

1. confirmation of the suitability of cartridge type analysis devices and the effectiveness of the techniques employed by comparison with superior infra-red analysis under the controlled laboratory conditions,

2. use of the load-speed measuring devices associated with load factor determination to permit proper comparison of toxic emissions for known load and speed with those of the same engine in a new condition thus to rigourously determine maintenance need, and,

3. determination of the relative merits of diesel-electric drives relative to direct diesel drives from an overall emission point of view.

7. Dust Hazards

Information has been found that indicates that carbon particles of the order of 0.05 microns are not only respirable but are retained in the alveoli of the lungs. This point is coupled with the fact that carbon particles generated in Diesel combustion can be of this order of magnitude. Further, Mining Research Centre personnel have expressed the concern that such dust can be expelled from Diesels because not all exhaust scrubbers are water-filled but rather many are catalytic in nature and therefore dry. Consequently, within the next two years, co-operating as much as possible with the Mining Research Centre, CEAL will attempt to instrument engines to determine the amount of carbon emitted under various equipment combinations and to determine the particle size distribution in order to assess the severity and incidence of this contaminant.

CONCLUSION

Thus a certification service capable of processing diesel-(and gasoline-) driven equipment up to a maximum power capacity of 400 BHP at 5000 RPM has been designed, constructed, and instrumented. Furthermore, the principles upon which certification is based are in the process of being refined by pursuing the various avenues of research which have been described above, in order that the optimum vehicle performance for Canadian mining conditions can result.

3.6 - DETAILED MEASUREMENTS OF EMISSIONS FROM SIX CUPOLAS

by

R. D. Warda and R. K. Buhr

ABSTRACT

Results of a detailed investigation of the amount and nature of effluent produced by cupolas are presented and discussed. The results were obtained during two-week periods spent at each of six iron foundries having cupolas with melting rates in the range 3 to 8 tons/hour. In addition to different melt rates, the foundries investigated differed considerably with regard to iron type and casting size, ranging from grey iron foundries producing municipal castings to a malleable shop producing components for the automobile industry.

Testing involved not only the measurement of all relevant gaseous and particulate effluent parameters, but also the monitoring of charging and melting practices.

Analyses of both the gaseous and particulate effluent data indicate the following:

1) variations in daily operation of cupola necessitate week-long test periods if meaningful results are required.

2) amount and type of both gaseous and particulate effluent vary systematically with the design and operation of the cupola.

3) gaseous effluent characteristics are affected primarily by coke-total air ratios and gas temperatures at the point of mixing with charge door air.

4) regarding particulate effluent, the cupola is both a transmitter and a generator, the transmitted component usually predominating.

5) suggestions made during testing to both reduce and identify the transmitted component of the particulate were highly successful.

Introduction

During 1971, the Foundry Section of PMD conducted a detailed study of cupola emissions. This study had two main objectives:

1) the design and assessment of the methodology of cupola emission testing, and

2) the accumulation of data of proven reliability on all aspects of cupola emissions which could be used not only for establishing and complying with air pollution codes, but also for developing new pollution abatement processes.

This program was carried out in two consecutive stages; summer field work designed primarily to obtain raw data, followed by data treatment and analysis.

Methodology

The scheduled field work program consisted of two-week test periods spent at each of five foundries. An unscheduled one week test was performed at a sixth foundry at the request of the local Ontario Air Management engineer. At each foundry the following functions were performed:

1) continuous measurement of temperature, velocity, and concentrations of CO and CO_2 of stack gases.

2) intermittent sampling of stack gases for measurement of CO, CO_2, O_2, NO_X and SO_X concentrations.

3) continuous isokinetic collection of particulate, and

4) assessment of all relevant cupola operating practices.

Subsequent to the completion of the field work, all field measurements were compiled and collected dust samples were subjected to size and ignition loss determinations as well as X-ray fluorescence and diffraction analyses.

Finally, completed parameter measurements were evaluated by statistical analysis and when possible by their incorporation in heat and material balances.

Results

Table 1 summarizes the data which has been compiled to date. The first two variables describe the cupola production and fuel consumption rates, respectively. The next two variables, in conjunction with Figure 1, characterize the particulate effluent. The remaining variables define the average properties of the exhaust gas after dilution by the air drawn in the charge door. Figure 2 illustrates the cyclic, systematic variations in temperature and concentration of CO and CO_2 and the relationship between these variations and the charging cycle.

Table 1: Summary of Cupola Emission Survey Results

VARIABLE	FOUNDRY					
	A	B	C	D	E	F
Melt Rate ton/hr	8	8	4.3	4.5	3	4.5
Melt/Coke Ratio	9:1	6:1	8:1-10:1	9:1	7:1	8:1-10:1
Dust Load lb/ton	43.6	15.5	17.9	8.2	26.7	4.8
Loss on Ignition %	15.3	21.5	37.6	17.5	22.8	26.4
Gas Temperature °F	350	1100	1350	1300	400	550
Gas Velocity FPM	1300	2500	2400	1400	2000	1100
NOx ppm.	<28	12	33	22	<28	14
SOx ppm.	264	710	481	288	276	288
CO Vol %	1.5	0.1	0.4	1.0	0.3	<0.5
CO_2 Vol %	5	8	8	10	3	7
O_2 Vol %	13	14	14	10	16	13

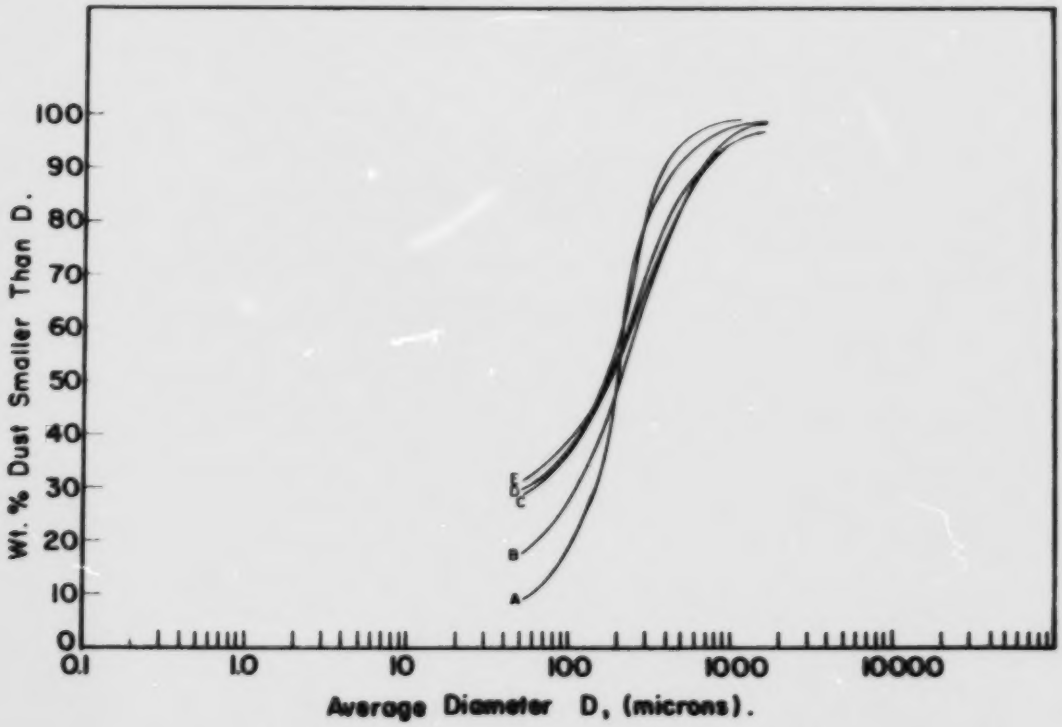


Figure 1. Size Distribution of Particulate Emissions.

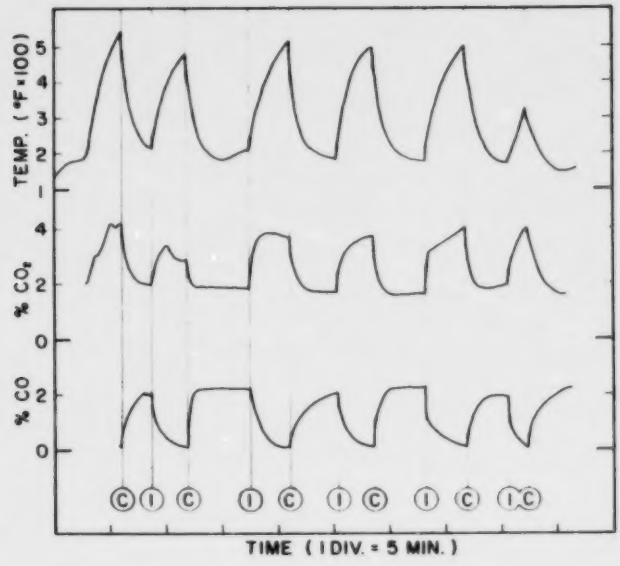


Figure 2. Variation of CO, CO_2 and temperature during charge cycle. "C" = charge. "I" = ignition.

Discussion

Considerable progress has been made toward the establishment of a cupola emission testing methodology. Both the particulate and gaseous effluent sampling trains, which were similar to those used at the Canadian Combustion Research Laboratory, operated satisfactorily in the adverse ambient conditions encountered. Severe constraints are placed upon the methodology by the design and operation of the cupola. Access limitations and stack design restrict the choice of sampling location. The nature of the cyclic variations in stack condition, as shown in Figure 2, demands not only responsive continuous sampling systems, but also careful choice of grab sampling intervals. Statistical analysis of effluent parameters indicates that test periods of not less than four days are required to ensure that reliable, representative results are obtained.

The cupola emission data accumulated during this survey strongly emphasize the extreme variations in cupola emission levels, not only from one foundry to the next, not only for a given foundry on a day-to-day basis, but also on a charge-to-charge time scale as shown in Figure 2.

Average dust production rates vary by almost an order of magnitude. The reason for this disparity is the fact that the cupola is both a transmitter and a generator of particulate. The amount of particulate generated per ton of metal melted is approximately equal for all cupolas; the difference in total emissions results from changes in the transmitted particulate. This suggestion was confirmed by changes in charging procedure undertaken at foundries A and F. Cupola personnel were requested to minimize loose dirt being charged. This resulted in a 60% reduction in particulate emissions at foundry A, but no detectable reduction at foundry F.

Figure 1 shows that significant differences also occur in the size distribution of the emitted particulate. These variations become more important as the average particulate size decreases and the cost of collection equipment increases.

Although analysis of the gaseous emission data is incomplete, the coke-total air ratio and the gas temperature at the charge door have been identified as two of the more important variables. Since the coke-air blast ratio is maintained within narrow limits, the variation in the coke-total air ratio is primarily a function of the rate at which air enters the cupola through the charge door. This rate depends on cupola construction, and varies from one to six times the air blast rate. The air drawn in the charge door influences all gaseous emission characteristics through the mechanisms of dilution and combustion. The latter phenomenon results from the spontaneous ignition of CO at the charge door, causing fluctuations in CO and CO_2 concentrations and temperature during each charging cycle, as shown in Figure 2.

Acknowledgements

The field work was carried out with the cooperation of the Department of Environment of the Province of Ontario and the foundry personnel. George Lee and Ray Fouhse of CCRL provided not only stack sampling expertise and equipment, but also assistance throughout the field work program.

3.7 - THE DESULPHURIZATION OF OIL BEFORE COMBUSTION

- A report of progress on the refining and desulphurization of low-grade residual oils and tars by the Engineering and Scientific Staff of the Hydrocarbon Group.

presented by

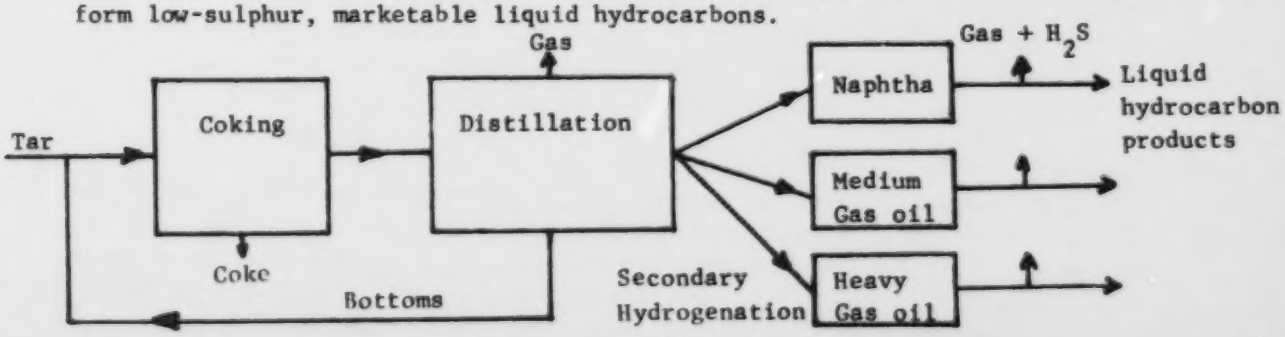
B. I. Parsons

The main objective of the Hydrocarbon Group is the development of catalytic hydrogenation and desulphurization systems for the production of clean fuels from low quality petroleum at reasonable cost. Virtually all of the experimental work of the group fits into some aspect of a cost-lowering vs effectiveness program. The basic technology for the production of clean fuels (from either low-grade oil or coal) by hydrogenation has existed since the 1930's. The demand now is for means of simplifying operating systems lowering pressures, minimizing coking and for cheaper catalysts.

Any chemical process is complicated on a large scale. The group is not attempting to investigate every step or manipulation along the way, rather, it has concentrated on selected areas. Considerable progress has been made during the past 18 months ....far more than has been made in the previous five, possibly 10 years. We believe, indeed, we now know, that desulphurization before combustion is possible on an industrial scale at reasonable cost.

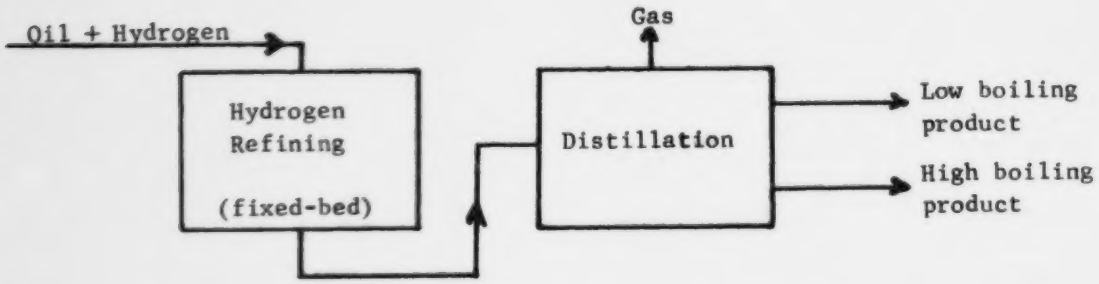
To begin with I would like to define what we mean by a "low-grade" oil. We mean an oil of which one-third tc two-thirds is undistillable, asphaltic or resinous hydrocarbon material. The sulphur concentration, on an as received basis, is 4 to 6 % by weight, nitrogen 1/2 to 1 %, oxygen 1/2 to 1 % and the concentration of chemically combined metals such as V, Ni and iron is generally in the range of 300 - 600 ppm. A good example of such an oil is the bitumen separated from the Athabasca Tar Sands. This material is, in fact, our standard experimental feed stock. Another example would be the residual oils from Venezuela.

The oldest procedure for upgrading fuels is a three-step process in which part of the high molecular weight asphaltics and resins are cracked by thermal coking, followed by distillation and the hydrodesulphurization of the vapours to form low-sulphur, marketable liquid hydrocarbons.



The only real improvement in this scheme that has taken place during the past thirty years has occurred in the distillation step. Mechanical improvements now permit vacuum separations of undistillable and distillable hydrocarbon up to the equivalent of 1000°F at atmospheric pressure compared to 800 - 850°F previously. On a commercial scale, once the separation of the distillable and undistillable material has been accomplished the problems are minimal. The naphtha and gas-oil fractions are desulphurized relatively easily at low pressures (700 - 1200 psi). Each stream must be handled slightly differently in conventional fixed-bed reactors to minimize gasification and coking. Catalyst life is measured in years, and catalyst cost is very small indeed. Almost every refinery in North America practises hydrodesulphurization of this secondary type in the preparation of feed stocks for gasoline reformers and hydrocracking units.

Another scheme for desulphurization is slanted primarily to fuel oil production and is mechanically, much simpler. The feed material is processed directly in a fixed-bed catalytic reactor at moderate pressures (1500 - 2000 psi).



At the present time this type of processing is restricted to heavy feed stocks containing low concentrations of chemically combined nickel and vanadium because the metals deposit onto the catalyst surfaces, poison the active sites and generally foul the operation. The catalysts so poisoned cannot be regenerated and must be replaced.

As a fixed-bed unit this type of process is not applicable to what we in Canada usually refer to as a low-grade oil. The athabasca bitumen, for example, contains 400 - 600 ppm of metals compared to 40 - 60 ppm for a low-grade, middle-east crude. From a global viewpoint, however, this relatively simple, direct approach is a workable system for a great many high sulphur crudes. In the past five years several desulphurization units of this type have been constructed, notably in Japan, for the production of 1 % sulphur fuels from 4 % sulphur middle-east crude. Catalyst life is reported to be of the order of six months to one year....where the metals content of the crude is of the order of 50 ppm.

1. Distillation - continuous vacuum unit

In a great many respects the success, or failure, encountered in a desulphurization research program depends on the distillation equipment. I am sure that you have noticed that distillation is common to both schemes....in fact, I should have shown a distillation step preceding both as well, as feed stock preparation is also a vital aspect of the Process Engineering. Most low-grade residuals contain temperature sensitive asphaltic material and the thermal history, topping and

blending of feeds has a profound effect on the rates of coking and polymer formation in subsequent steps. The importance of being able to simulate commercial stripping in the manipulation of the feed stocks and products simply cannot be overemphasized.

The Engineer in charge of distillation for the group is Mr. John Denis. He designed a pilot-scale, continuous vacuum unit which was put through preliminary tests at Booth Street, then reconstructed at our new facilities at Bells Corners, and is just now coming into its own. Recent modifications made to the unit have extended the working upper limit from 850°F to 1000°F equivalent temperature at atmospheric pressure. During the past year the unit was successfully calibrated against industrial standards and various feeds and products for, and from, the desulphurization program separated into their component fractions. All the gas-oils and diluents used in the program, of course, also originate from this very versatile piece of equipment. I have said all that relatively quickly but please realize that this aspect of the program represents a tremendous amount of work.

2. Liquid Phase Thermal Hydrocracking

On the more direct processing side, a large part of the experimental effort has been concentrated on investigating the prospects of substituting thermal hydrocracking for coking in the three-step desulphurization scheme. Coking, per se, is a highly undesirable process from almost every point of view. It is wasteful of the resource and produces a high-sulphur coke for combustion purposes. In the coking process the best of the resin and asphaltic material in the tar is converted by cracking and hydrogen abstration into distillate hydrocarbons by the direct application of heat, and the more refractory components in the feed degenerate to coke. Conversion of the +1000°F fractions to distillable hydrocarbons rarely exceeds 45 - 50 % and the sulphur content of the coke usually occurs in the range 6 to 8 % by weight with the coker distillate running approximately 4 %.

The basic principles for successful thermal hydrocracking were established by Bergius near the turn of the century for the liquification of coal and pitches. Various engineering studies were later undertaken in Germany and Britain before the last war, and by the U. S. Bureau of Mines after the war. In our mechanical adaption of all these thoughts of decades ago, the oil is heated in the presence of hydrogen at 1000 psi, pumped once through a long narrow pipe reactor (without benefit of conventional catalysts) then separated into distillable and undistillable fractions. All the chemical reactions occurring in the coking process are caused to happen in a hydrogen atmosphere with a view to minimizing coke formation. There are very definite limits, of course, as to how far the thermal bludgening of hydrocarbons can be forced in any atmosphere before some coke results. In the operation of the system one approaches this limit as closely as possible to maximize yields.

During the past year the continuous thermal hydrocracking of Athabasca bitumen has been thoroughly investigated on a pilot plant scale by the Petroleum Processing Section under Mr. Bill Merrill. Considerable experimentation has been required and extensive modifications and adaptations have been undertaken in the light of experience ....with considerable success. Mr. Merrill and his staff have shown, for example, that up to 70 % of the +1000°F bottoms can be converted to

distillable hydrocarbons by thermal hydrocracking. This is to be compared to a maximum of 50 % conversion by delayed coking. In the perspective of a 100,000 bbl per day plant this represents:

1. a daily increase of 9000 bbl of marketable hydrocarbon
2. a daily reduction of 9000 bbl of coke or pitch which must be burned (and the sulphur recovered) to keep the process in overall thermal and economic balance.

There are many operational tricks involving diluents, linear liquid velocities and length to diameter ratio, which make an interesting Engineering story but are clearly beyond the scope of the present summary.

3. Catalytic Hydrocracking

In addition to the study of purely thermal hydrocracking the group has also made considerable progress on the development of the "all catalytic" process for the refining of high metal residuals. The problems here are partly mechanical and partly chemical or catalytic. It has been clearly demonstrated, in both the United States and in Japan, that desulphurization and metal deposition on the catalyst occur simultaneously. For high sulphur, high metals feed stocks catalyst life will be short....of the order of 50 to 100 hours. Catalysts involved must be cheap and a means must be provided in the mechanical arrangement for adding and removing catalyst because of the great difficulty of operating with short stream times.

The simplest mechanical arrangement for adding and removing catalyst "on-the-go" so to speak occurs with a fluidized bed. Over the past few years a liquid phase fluidized bed system has been assembled, modelled mostly on German experience in coal paste hydrogenation. The basic units of this system were designed by Dr. Walter Herrmann. In Germany, liquid phase systems were operated at quite high pressures, of the order of 5000 - 10000 psi, and any unreacted material passing through the reactor was recycled. There is no question that both the yield and quality of products from a hydrogenation system improve at higher pressures, but the capital cost today of the equipment involved reduces the prospects for a high pressure process. All recent experiments have been undertaken at 1000 psi with the occasional run up to 2000 psi. At these lower pressures, the recycle of unreacted material is at present impractical because of the effect on catalyst life. The group effort has been concentrated on the development of a once-through liquid phase system using low-cost catalysts.

We have made some progress on these concepts but there is some left to do yet. Mr. Merrill and his staff have improved the operation of the pilot plant system and the ball has been tossed back to the catalyst development laboratory for the preparation of suitable catalysts. In this area we are attempting to devise a means of mulling active catalysts on to the surface of a cheap inert base. So far we have been able to lower the concentration of active metals by a factor of 4 and still maintain a high proportion of effectiveness.

The combination of low pressure, cheap catalysts, and a means of adding and removing catalyst on-the-go, in our opinion, offers the best prospect for solving the desulphurization problem. The limited number of experiments that we have undertaken indicate higher yields, cleaner distillates, and only small amounts of relatively low sulphur pitch being produced compared to large amounts of high sulphur coke.

3.8 -CCRL - FUEL EFFICIENCY PROGRAM

by

E.R. Mitchell

Laboratory Fuel Efficiency Testing

One of the first responsibilities of a fuel oriented group is the subject of "fuel efficiency". Indeed, in the early days of the "Fuel Testing Laboratories" later known as the Fuels Division of Mines Branch (dating from about 1922 to 1949), this was a major laboratory activity. In 1950 it was extended first to efficiency testing of DPW heating plants then to testing of other government plants and industrial power plants.

Gradually, the laboratory activity was directed to more serious combustion and flame research leading to the present program of the CCRL (Canadian Combustion Research Laboratory).

Field Activity

The field tests have been variously described as heat-balance tests, combustion performance tests, acceptance tests and fuel efficiency tests. The latter title incorrectly suggests flame and combustion efficiency separate from the furnace or boiler heat exchange efficiency and for this reason it is less popular than the other titles.

In any event, they serve three purposes. First, they provide the heating plant or power plant with a permanent record of operating parameters to obtain the highest fuel efficiency with a minimum of air pollution. Second, they provide a reliable evaluation of the degree of excellence of industrial burner and furnace designs. Third, they provide a basis for directing flame and combustion research in the laboratory to serve industrial needs.

The results of several hundred individual boiler efficiency tests are summarized in Tables 1 and 2.

The number of heat-balance or efficiency tests varies from year to year but ranges from a low of 10 to a high of 30 for a heating season.

Advancing Methodologies

All combustion programs have been hampered by inadequate sampling and analysis procedures for the numerous parameters involved. Thus, over the years the CCRL has improved methodologies and has applied sophisticated sampling and analytical procedures.

Combustion Handbook for Canadian Fuels

The result of improving test procedures has been a heavy demand for heat-balance testing which, of necessity, has taken into account the interests of industry and Consulting Engineers who depend upon this subject for their income. As a contribution to them and to government agencies a "Combustion Handbook for Canadian Fuels" volume 1 for fuel oils has been published and volumes 2 and 3 for coal and gas fuels are in process of being published.

This handbook presents precise combustion computations in graphical form as well as heat-loss computations for heat-balance or efficiency determinations.

This has become a classic in the industry. Another classic is the Boiler Acceptance Tests at the Cliff St. Central Heating Plant, Ottawa, August 1966, by F.D. Friedrich.

TABLE 1

Typical Performance Data at Minimum Pollution Emissions*

Shop-Fabricated Fire-Tube Package Boilers

	Package boiler type		Two-pass		Three-pass				Four-pass
	Fuel used:		No. 6 Fuel Oil		Natural Gas		No. 2 Fuel Oil		No. 6 Fuel Oil
	Boiler horsepower and (lb steam/hr)		250 (8700)	350 (12,200)	250 (8700)	350 (12,200)	250 (8700)	350 (12,200)	150 (5200)
Full	Flue gas temperature	°F	450	387	481	440	490	426	398
	Combustion air temperature	°F	71	76	65	71	87	89	82
	CO_2 in flue gas	%	11.4	13.2	10.5	10.2	13.1	13.6	13.3
	Excess air	%	38.5	20.5	10.0	13.0	15.0	12.0	21.0
	Losses - dry gas	%	9.5	6.8	7.4	6.8	8.1	6.6	7.0
	- combustion of H_2	%	6.6	6.4	11.9	11.7	7.1	6.9	6.1
	- radiation	%	1.9	1.5	1.9	1.5	2.0	1.5	2.7
	Efficiency	%	82.0	85.3	78.8	80.0	82.8	85.0	84.2
Half	Flue gas temperature	°F	410	352	-	371	449	380	374
	Combustion air temperature	°F	72	78	-	77	88	87	86
	CO_2 in flue gas	%	8.5	11.8	-	9.6	11.0	11.4	10.4
	Excess air	%	83.0	34.0	-	19.0	36.0	32.0	53.6
	Losses - dry gas	%	11.5	6.7	-	5.8	8.7	6.8	8.0
	- combustion of H_2	%	6.4	6.3	-	11.3	7.0	6.8	6.0
	- radiation	%	3.4	3.4	-	3.0	3.4	3.2	4.9
	Efficiency	%	78.7	83.6	-	79.9	80.9	83.2	81.1
Low	Flue gas temperature	°F	370	344	372	343	391	364	344
	Combustion air temperature	°F	70	76	69	90	79	77	86
	CO_2 in flue gas	%	8.6	9.2	7.2	7.4	10.9	11.1	10.2
	Excess air	%	81.3	70.0	53.0	51.0	37.0	35.0	56.4
	Losses - dry gas	%	9.8	8.3	7.7	6.4	7.5	6.8	7.2
	- combustion of H_2	%	6.4	6.3	11.4	11.1	6.8	6.8	5.9
	- radiation	%	6.0	4.0	6.5	6.5	6.5	5.0	8.0
	Efficiency	%	77.8	81.4	74.4	76.0	80.7	81.4	78.9

*Results of heat balance tests by the Canadian Combustion Research Laboratory, Mines Branch, Department of Energy, Mines and Resources.

TABLE 2

Actual Thermal Efficiency of Steam Boilers and High-Temperature Water (HTW) Generators Measured at Minimum Pollution Emission*

Fuel	Oil		Natural Gas		Coal	
Fuel Firing Rate	low	high	low	high	low	high
High-pressure steam boilers (100-150 psi)						
(a) Originally coal-fired						
100,000 lb/hr - Field Erected	87.3	85.8	83.6	82.9	-	83.36
60,000 " " "	83.8	81.5	80.4	77.9	-	77.67
33,000 " " "	76.6	80.0	75.9	78.1	-	-
25,000 " " "	-	-	-	-	-	81.13
21,000 " " "	82.5	82.2	-	-	-	-
16,800 " " "	79.6	79.8	77.6	76.6	-	-
15,000 " " "	83.6	83.2	-	-	-	-
(b) Installed with oil-gas						
80,000 Field Erected	-	83.8	-	79.3		
60,000 Package	83.2	82.0	80.2	77.4		
50,000 (oil only) "	82.3	81.0	-	-		
40,000 "	80.5	81.0	78.5	78.7		
30,000 (oil only) "	82.5	82.9	-	-		
25,000 (gas only) "	-	-	79.0	79.0		
20,000 (oil only) "	81.7	82.9	-	-		
(c) Low-pressure steam (15 psi)						
8,625 lb/hr package fire tube (gas only)			77.0	81.1		
High-temperature water generators (HTW)						
Converted from coal firing						
30.0×10^6 Btu/hr	82.2	80.7	79.0	78.3		
Installed with No. 2 oil-gas						
16.6×10^6 Btu/hr	86.0	86.8	82.4	83.8		
Medium-temperature water generators (MTW)						
25.1×10^6 Btu/hr package fire tube	-	-	82.5	85.6		
16.7×10^6 Btu/hr " " "	85.8	85.4	-	-		
6.7×10^6 Btu/hr " " "	-	81.3	-	-		
5.02×10^6 Btu/hr " " "	-	-	80.3	82.7		

*Results of heat balance tests by the Canadian Combustion Research Laboratory, Mines Branch, Department of Energy, Mines and Resources. These are measured values on actual boilers and should not be interpreted as a general guide for efficiency vs boiler size.

3.9.1 - FLAME RESEARCH

BLUE FLAME

by

T. D. Brown

- - - -

ABSTRACT

The characteristics of twelve burners supplied to the CCRL by the Oil Heating Association of Canada have been determined in a 10 in. flame tunnel furnace for comparison with the performance of a prototype Blue Flame Burner manufactured in Sweden. The designs all incorporate a retention or swirl head in which the input air is given a rotational momentum. The blue flame burner shows a much greater rotational component than any of the yellow flame burners and the increased recirculation mass flow leads to fuel vaporization prior to combustion and to a lower flame temperature. Consequently, low excess air combustion without soot and carbon monoxide formation at minimum NO_x production can be achieved.

BLUE FLAME COMBUSTION - 1971

An examination of the contribution of typical oil fired retention head domestic burners has been carried out by CCRL. Twelve burners were supplied by the Oil Heating Association of Canada as being the current designs which offered the best performance in terms of flame stability under varying draft (external pressure) conditions. The term "retention head" refers to the design of the air register situated at the end of the blast tube surrounding the oil line.

Typical pollutant emission levels from these burners were found to be:-

NO:	1.2 lb/1000 lb fuel
SO_2:	7 lb/1000 lb fuel
CO:	0.5 lb/1000 lb fuel
Particulates:	2.0 lb/1000 lb fuel.

All the burners tested were conventional yellow flame systems.

Further points which emerged from the survey were:-

a) The emission of CO and particulates during steady running--as reported above--could be increased by a factor of ten during the period immediately following the initiation of a start up or shut down sequence. This change in emission was reduced to a threefold increase by inclusion of a stop valve in the fuel supply line.

b) The aerodynamic flow patterns generated by retention head burners was not greatly different from that of an enclosed plane jet; there was no evidence of a central recirculation core in the system. It appears that the retention head acts only as a turbulence generator in the flow, the micro scale mixing is improved but no use is made of the overall aerodynamic flow other than via external recirculation. Systems of this sort do not permit operation at low excess air levels without excessive soot formation.

The design of prototype blue flame systems in the laboratory has been based on a requirement for large amounts of central recirculation generated by swirl heads situated in the blast tube surrounding the oil nozzle. The oil spray is located in such a position as to ensure that the fuel is directed into a region of reverse flow and not into the high shear region of the forward flow as is usually the case. The purpose of this configuration is to permit complete evaporation of the fuel prior to combustion and thus avoid the high temperature soot formation that is responsible for the characteristic yellow colour of conventional flames.

Three swirl heads producing a range of central recirculation mass flows have been examined. The results indicate that in increasing the central recirculation mass flows to a level greater than 10% of the total air input leads to production of a blue flame. Further increases give a more stable system and permit the use of a wider range of atomizing nozzles.

Bibliography

Some Performance Characteristics of Flame Retention Head Domestic Burners, by T. D. Brown, Internal Report FRC 72/8-CCRL.

3.9.2 - FLAME RESEARCH

LOW NO_x FLAMES

by

T. D. Brown and G. K. Lee

- - - -

ABSTRACT

NO formation in combustion systems can be represented by an equation of the form:

$$\frac{d(NO)}{dt} = A\, e^{\frac{-E}{RT}} \left[O_2\right]^{1/2} \left[N_2\right]$$

It can be seen that factors which will limit the extent of this formation will be

a) Reduction in Oxygen Concentration (Excess Air Level)
b) Reduction in Flame Temperature
c) Reduction in Reaction Time.

The first factors are opposed in the sense that decreased excess air levels lead to increased flame temperatures; the most effective reduction in NO formation is not necessarily achieved by reducing the excess air level which brings as a side effect a possibility of incomplete combustion.

A recent series of experiments at CCRL have been conducted to examine the effects of external flue gas recirculation on the production of NO. The effect of flue gas recirculation is to reduce the flame temperature and also, because of the increased flow through the combustion system, to make low excess air level more easily achieved without incomplete combustion.

LOW NO_x FLAMES - 1971

The formation of nitric oxide in combustion systems occurs by a chain reaction mechanism:

$$O_2 \rightleftharpoons 2O$$
$$N_2 + O \rightleftharpoons NO + N$$
$$O_2 + N \rightleftharpoons NO + O$$

The rate expression for the reaction takes the form:

$$\frac{d(NO)}{dt} = k_1 e^{-\frac{E_1}{RT}} \left[O_2\right]^{1/2} \left[N_2\right] - k_2 e^{-\frac{E_2}{RT}} \left[NO\right]^2 \left[O_2\right]^{1/2}$$

Calculations of the yield of nitric oxide from a plug flow reactor at various oxygen concentrations and temperature levels indicate that for oxygen partial pressures greater than 0.01 the temperature is the dominant variable.

Temperature °K	Residence Time	O_2	NO Yield
2000 - 1900	0.515 sec	5%	400 ppm
"	0.515 sec	1%	200 ppm
1900 - 1800	0.65 sec	5%	75 ppm
"	0.65 sec	1%	34 ppm

Methods of control of the formation of nitric oxide in operational systems that are based on these kinetic arguments are:

Low Excess Air Combustion
Decreased Boiler Load
External Flue Gas Recirculation.

The effect of external flue gas recirculation (gas temperature 500°F) is to increase the thermal load on the fuel. The recirculated flue gases contain approximately 3% oxygen and act as an inert material in the combustion process since they must be heated to the effective flame temperature; the flame temperature is consequently reduced.

The magnitude of these three effects has been examined at CCRL in a pilot scale experimental boiler burning No. 2 Fuel Oil.

1) Low Excess Air Combustion

O_2 in Flue Gases %	NO Emission lb/1000 lb Fuel
3	1.05
2.8	0.92
2.0	0.90
0.5	0.72
0.25	0.73

2) Boiler Load

Firing Rate lb/hr	O_2 in Flue Gases %	NO Emission lb/1000 lb Fuel
119	3	1.05
"	2	0.90
"	1	0.72
85	3	0.77
"	2	0.59
"	1	0.48

3) External Flue Gas Recirculation

Firing Rate lb/hr	O_2 Level %	Recirculation Ratio* %	NO Emission lb/1000 lb Fuel
119	3	0	0.98
"	3	15	0.81
"	3	23	0.70
"	3	31	0.55

$$*\text{Recirculation Ratio} = \frac{\text{Mass of Air Recirculated}}{\text{Mass Flow Rate Through Combustion Chamber}}$$

For external recirculation to be an effective measure in the reduction of NO emissions it is essential that the flue gases should form part of the flame system. It is likely therefore that a revision to the recirculation ratio parameter should be made to incorporate the magnitude of the thermal recirculation as well as the mass recirculation. Plainly an adiabatic recirculation at flame temperature would not produce any major change in flame temperatures despite the magnitude of the mass recirculation.

One particular advantage of external flue gas recirculation is the increase in burner momentum that occurs. This can be made to lead to improved aerodynamic mixing in the combustion chamber and consequently low excess air combustion without soot formation should be possible. This combination of the two methods of control of NO formation is likely to give minimum NO emissions.

Bibliography

The Formation of Oxide of Nitrogen in a Combustion System, by D. Thompson, T. D. Brown and J. M. Beér. Presented at the A. I. Chem. E. Annual Meeting, Session on Air Pollution Related Combustion Research, Atlantic City, August 1971.

3.9.3 - FLAME RESEARCH

THE COMBUSTION OF COAL-IN-OIL SLURRY

by

G. K. Lee

- - -

ABSTRACT

A coal-in-oil combustion research project was initiated in December 1971 with technical support from Ontario Hydro and financial assistance from the Winter Works Program through the Metals Reduction and Energy Centre. The purpose of this research is to demonstrate the technological feasibility of burning coal-in-oil slurries as a fuel for steam raising.

In the two months since the project started, a pilot-scale hydraulic system for blending and pumping coal-in-oil slurries has been designed and installed, and a low-pressure, air-atomizing oil burner has been modified to burn this type of fuel. Preliminary experiments with the fuel handling and combustion systems have been completed and design changes are now in progress to optimize the performance of various system components.

Future research will include detailed evaluations of the combustion, corrosion and pollution potential of a variety of coals in either crude or distillate oil.

PROJECT BACKGROUND AND PROGRESS REPORT

In recent years the escalating demand for energy, coupled with the enactment of stringent air pollution regulations, has resulted in the widespread use of low-sulphur fuels by Canadian industry. At the same time, traditional supplies of low-sulphur coal from the U.S. have rapidly declined causing a sharp increase in the consumption of low-sulphur oil and gas. Unfortunately, our easily accessible gas and oil reserves are limited, and until large blocks of nuclear power are available, there seems to be no alternative but to continue generating a substantial portion of our energy requirements from coal. It is not surprising then that considerable interest is now being shown, in methods of utilizing the vast low-sulphur coal resources, of western Canada, including the large tonnages of waste from coking coal beneficiation plants.

It is in this context that research on the feasibility of burning coal-in-oil slurries was initiated in December of last year, with technical support from Ontario Hydro and financial assistance from the Metals Reduction and Energy Centre of the Mines Branch. This approach, if successful, would permit the friable, dusty coals of western Canada to be pipelined over long distances at low cost, and burned at destination with minimal handling and pollution.

The concept of a coal-in-oil fuel is not new. According to papers dating back to 1879, mixtures of coal and oil have been burned experimentally for periods up to a week, with varying degrees of success, in a number of combustion systems including blast furnaces, marine boilers and even diesel engines. These papers give many details of the fuel preparation systems used, but the combustion aspects of the tests are not well documented.

For this reason, the major part of our combustion research program is being directed toward the development of suitable burners and a study of the many parameters necessary to produce reliable, low pollution flames.

During the first two months of the program a pilot-scale preparation and handling system was designed and constructed, and hydraulic studies were conducted on mixtures of No. 2 fuel oil containing between 30% and 50% by wt, of coking coal that had been pulverized to 80% through 200 mesh. The hydraulic studies indicated that this coal-in-oil slurry can be blended, suspended and pumped without difficulty and that any sedimentation during week-end storage can be readily fluidized by normal mechanical mixing and air bubbling. In addition, no pipeline blockage has been experienced with flow velocities over 2 fps although control valves other than the ball-type tended to plug with coal after a few minutes.

Preliminary combustion experiments, using an undersize combustion chamber mounted on the flame tunnel furnace, have shown that stable coal-in-oil flames can be obtained using a modified air atomizing oil burner, capable of firing slurry at 12 gph. These experiments provided the criteria necessary for both the design of a larger chamber that is being fabricated by the Technical Services Division and the selection of more reliable components on the hydraulic system.

After demonstrating the ability of the fuel handling and combustion system to operate continuously, while burning a high-volatile bituminous coal, research studies will be undertaken to evaluate the combustion and pollution emission characteristics of a variety of Canadian coals including lignite, coking coal rejects and non-coking coal suspended in either crude or distillate oil.

3.9.4 - FLAME RESEARCH

NEXT GENERATION OF BURNERS

by

F.D. Friedrich

- - - - -

ABSTRACT

The next generation of burners will be characterized by minimum pollution emission. It will produce virtually no CO, unburned hydrocarbons, or soot and, at least while burning oil or gas, it will operate with excess air in the range of 3%, equivalent to 0.6% O_2 in the flue gas. At the same time, NO emission will be reduced by at least 50% to between 45 and 200 ppm depending upon furnace conditions. To maintain consistently low NO, it is likely that forced recirculation of combustion gases to the burner may be added. It is anticipated that this high level of performance will be achieved by means of high combustion air pressure (15 in. of water or more) coupled with scientifically selected methods for generating high levels of turbulence. It is expected that flames will be more transparent than in the past; some oil flames will be blue.

The present, well-proven technology for fuel oil atomization and coal pulverization will probably be used in the next generation of burners.

Flame research in recent years has shown that the process of combustion is dominated by the fluid mechanics of the system rather than by chemical kinetics or heat transfer. This research has also led to the development of reliable techniques for measuring flame aerodynamics and thermodynamics. Thus, the diffusion mechanism can now be controlled in quantitative terms by means of swirl, or shearing jets, and it becomes useful to develop swirl parameters.

PROGRESS TOWARD THE NEXT GENERATION OF BURNERS IN 1971

In our struggle against pollution it is natural that we should take a hard look at a major source of air pollution; namely, fossil-fuel burners for heating, steam-raising and power generation.

The present generation of burners has evolved empirically, with highest priority being given to safety, reliability, automation and cost. These priorities have largely been achieved, but control of flame aerodynamics is limited and fuel-air mixing is less than ideal. Present-day burners generally require fairly high excess air, particularly on turn-down. Residual oil burners, for example--to simplify this discussion only oil burners will be referred to--require at least 15% excess air except under special circumstances. Flames are usually yellow and ragged, although fairly quiet. Atomization, and therefore flame performance, tends to deteriorate as the burner is turned down. Turn-down is generally limited to about 20% of full firing rate.

Typically, for a residual oil burner pollutant emission is as follows:

- up to 0.25% of fuel unburned
- 100 to 500 ppm of NO_x, increasing with the size of burner and furnace
- up to 500 ppm of CO
- fairly high levels of SO_3, up to 70 ppm for oil containing 3% sulphur.

There are now on the market a few oil burners, generally of small capacity, that offer much better performance in terms of pollutant emission, for example:

- negligible unburned fuel
- 50% reduction in NO_x
- negligible CO
- negligible SO_3.

The formation of SO_2 is essentially dependent on the sulphur concentration in the fuel, therefore no improvement can be expected through burner design. These burners have the further advantage of being able to operate at 3 to 5% excess air, that is, less than 1% excess oxygen.

Burners having the characteristics just described are fore-runners of the next burner generation, and are generically known as "blue flame" burners, because when burning light oil the flame is blue, like a natural gas flame, rather than yellow. When burning heavy oil the flame is not blue, but it is substantially more transparent than the flame from a conventional burner, and it has a substantially lower emissivity.

As stated previously, there are a few blue flame burners now on the market. These are not tremendously popular because they are expensive, often they are noisy, they are generally limited to small capacities, and sometimes

they have a relatively high running cost. Their development has also been hindered by the fact that a successful design is largely a matter of luck. The empirical method of design seems to have reached the limit of its capabilities with the present generation of burners.

An obvious question is: "What's so difficult about building a better burner?"

This is best answered by first considering the principles of operation of a present-generation burner. Figure 1 shows a typical construction. Basically, the burner consists of a windbox with some sort of register to direct the combustion air uniformly into a throat built into the wall of the furnace. An oil gun, located on the axis of the throat, carries oil and the atomizing medium, usually steam or compressed air, to the atomizing nozzle, which ejects a conical spray of oil droplets into the combustion air stream. Devices are added to ignite the air-oil mixture, to control the flow of oil and air according to heat demand, and to automatically shut off oil flow in case a dangerous situation arises.

Burners such as this operate with a relatively low windbox pressure; sometimes 6 in. W.C. at full load, more commonly about 2 in. W.C. Because the burner geometry is fixed, windbox pressure drops to near 0 when the burner is turned down to minimum firing rate. The air register may be designed to impart swirl, that is, angular momentum, to the air entering the throat, but with the low level of windbox pressure available, the angular component is very weak.

Years ago burner manufacturers discovered--empirically, of course--that performance could be substantially improved by installing a diffusor. This is a disc in the form of a shallow cone, usually slotted or perforated. It is mounted on the oil gun just upstream of the nozzle. It was only about fifteen years ago that work at the International Flame Research Foundation clearly demonstrated the reason for the value of a diffusor. It was shown that the bluff-body effect of the diffusor sets up, in its wake, a small recirculation zone, which brings hot combustion gases back against the direction of air flow into the fuel-air interface. The heat and turbulence from these recirculated gases helps vapourize the fuel, initiates and stabilizes ignition, and improves mixing.

The existing examples of the next generation of burners mentioned previously can be compared to the diffusor in that the improved results are obvious, but the causes are not. It is known that improved combustion can be achieved, that is, blue flame conditions can be reached or approached, if there is a fairly high rate of heat transfer into the initial fuel-air interface, and if a very intimate mixing of fuel and air is achieved. It is also known that these conditions may be accomplished by modifying the burner aerodynamics. For example, by increasing the swirl of the combustion air, or by modifying burner

geometry, or both, the size and vigour of the recirculation zone can be substantially increased. This leads to greater heat transfer into the fuel spray, and increased turbulence, which should mean better vapourization and better mixing.

However, these measures can easily be overdone. A wrong combination of swirl and burner geometry can cause the air stream to separate from the oil spray. A recirculation zone which is too large or too low in temperature will result in poor combustion. An improper aerodynamic pattern or too high a temperature near the nozzle can lead to coke formation on the nozzle. The foregoing are only some examples.

Thus, the difficulties in building better burners stem from the fact that while there are a number of parameters which can improve combustion, each of these can be misapplied, with disastrous results. Before burner designs can be improved in a predictable fashion, these parameters must be thoroughly and accurately quantified. This is not easy to do in a flame at 3000°F.

The flame research program of the CCRL is designed to carry out the process of quantification. Major research facilities, such as the 1-metre tunnel furnace and the necessary water-cooled aerodynamic probes, have already been obtained. Because the work involves converting combustion from an art to a science, progress will be slow, but the result will be a substantial reduction in air pollutants emitted by a major source.

In summary, it appears likely that the next generation of burners will be characterized by

- operation at very low excess air
- negligible emission of unburned hydrocarbons, CO, and SO_3
- substantially reduced emission of nitrogen oxides.

SO_2 will have to be controlled by other means. Disadvantages of the next generation of burners will probably be

- higher horsepower for combustion air fans
- noise problems
- reduced heat transfer due to lower flame emissivity.

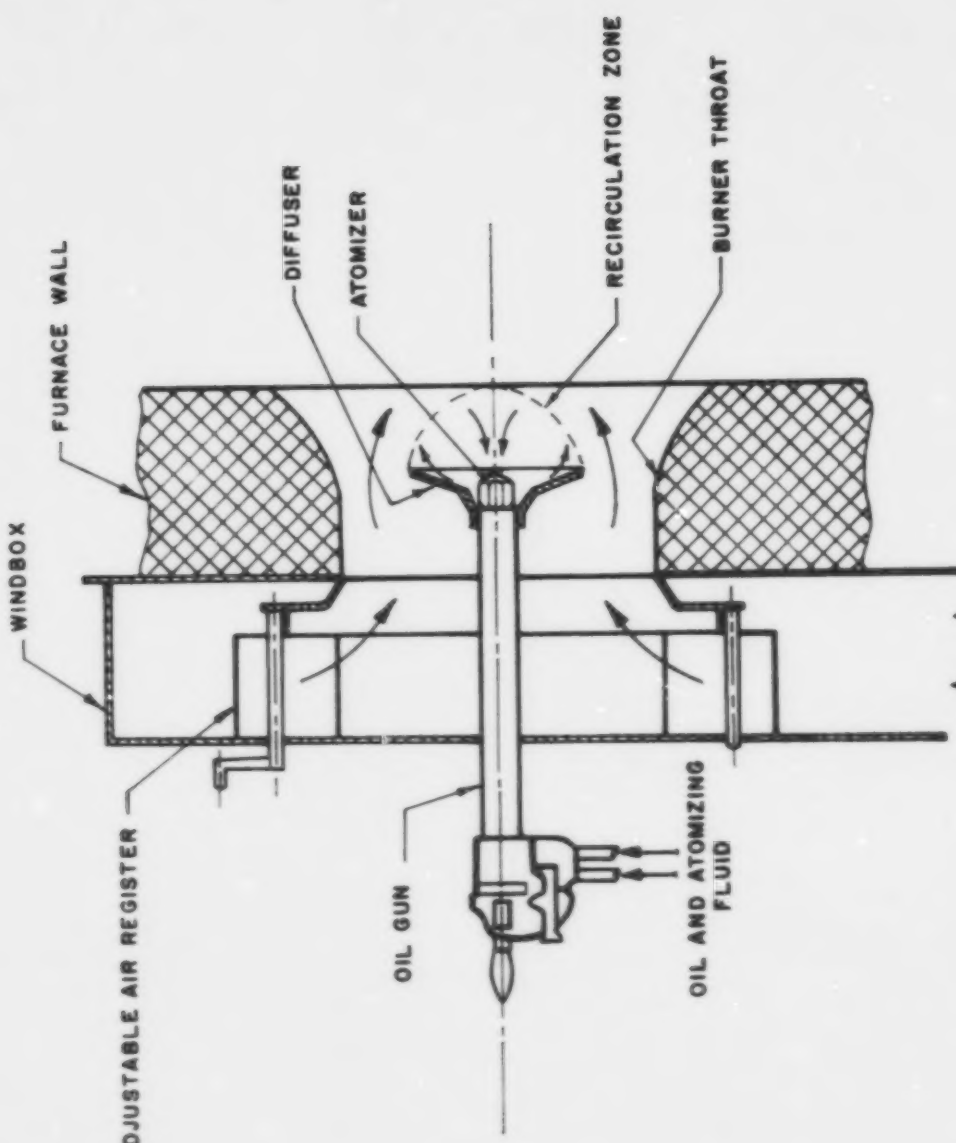


Figure 1. Schematic view of a typical present-generation oil burner.

3.9.5 - FLAME AND AIR POLLUTION RESEARCH BIBLIOGRAPHY

1971 PUBLICATIONS OF THE CANADIAN COMBUSTION RESEARCH LABORATORY

Number	Title	Author	Released for Distribution
FRC 71/7 CCRL	The CCRL Tunnel Furnace-Design and Application. Presented to International Flame Research Foundation Second Members Conference IJmuiden, Holland May 13-14, 1971	F.D. Friedrich E.R. Mitchell G.K. Lee H. Whaley	Mines Branch RS 104
FRC 71/15 CCRL	Combustion Performance of a Western Canadian Crude Oil - Presented to ASME Winter Annual Meeting, Washington, D.C., Nov. 28 - Dec., 1971	G.K. Lee F.D. Friedrich E.R. Mitchell R.G. Draper	ASME Paper 71-WA/CD3
FRC 71/17 CCRL	Measured Suspended Particulate Levels in an Oil Refinery Boiler Complex	H. Whaley D.G. Savignac	Industrial Confidential Mines Branch IR 71-18
FRC 71/20 CCRL	Equipment for Incineration of Municipal Waste - Presented to "Pollution: Mission Possible", Toronto 10 February 1971	F.D. Friedrich	Mines Branch TB 134
FRC 71/24 CCRL	Air Pollution in Canada from Fuel Combustion: 2nd Addendum to Mines Branch Information Circular IC 211 - Prepared for OECD Joint Group on Air Pollution from Fuel Combustion	E.R. Mitchell	Restricted Distribution until published by OECD
FRC 71/21 CCRL	The Incineration of Polymers - A Combustion Engineer's Viewpoint. Presented to 54th Canadian Chemical Conference and Exhibition "Symposium on Polymers and the Environment", Halifax, Nova Scotia May 31 - June 3, 1971	F.D. Friedrich	Mines Branch TB 135

FRC 71/34 CCRL	The Dispersion of Smelter Plumes in the Sudbury Area	H. Whaley G.K. Lee	Industrial Confidential Mines Branch IR 71-37
FRC 71/36 CCRL	Combustion and Fouling Characteristics of Two Canadian Lignites. Presented to ASME Winter Annual Meeting Washington, D.C. Nov. 28 - Dec. 2, 1971	F.D. Friedrich G.K. Lee E.R. Mitchell	ASME Paper 71-WA/CD3
FRC 71/42 CCRL	Boiler Performance Tests, Central Heating Plant, Maximum Security Institution, Millhaven, Ontario February 15-19, 1971	R.G. Fouhse B.C. Post	Limited Distribution
FRC 71/46 CCRL	The Next Generation of Burners - Presented to Ontario Section, Air Pollution Control Association Elgin House, Muskoka September 12-14, 1971	E.R. Mitchell F.D. Friedrich	Yes
FRC 71/67 CCRL	Laboratory Evaluation of the Huczka Filter	G.K. Lee	No Industrial Confidential
FRC 71/80 CCRL	Fuel Consumption and Air Pollution Trends in Canada 1965-1980	E.R. Mitchell	Mines Branch IC 279
FRC 71/83 CCRL	The Combustion and Fouling Characteristics of "washed" Bienfait Lignite - A Preliminary Assessment	G.K. Lee	Addendum ASME Paper 71-WA/CD3
Mines Branch Information Circular IC 268	Only People Pollute	E.R. Mitchell	CIMM Journal
Mines Branch Information Circular IC 269	Inventories of National and International Air Pollution	E.R. Mitchell	Yes
Air Pollution Control Association Paper APCA 71-132	A Study of the Meteorological Conditions Which Developed a Classic "Fumigation" Inland From a Large Lake Shoreline Source - Presented to 64th Annual Meeting of APCA. Atlantic City, N.J.,	M.S. Hirt L. Shenfeld G.K. Lee H. Whaley S. Djurfors	Mines Branch RS 106

Mines Branch Research Report R 234	The Thermal Destruction of DDT-Bearing Powders	G.K. Lee F.D. Friedrich B.C. Post H. Whaley	Yes
Eighth World Energy Conference Paper 2.3-85	The Dispersion of Multiple Plumes From a Large Thermal Generating Station	H. Whaley L. Shenfeld G.K. Lee M.S. Hirt S.G. Djurfors	Yes
Mines Branch Technical Bulletin TB 136	A Plasma Furnace for Ashing Micro-Samples of Particulate Matter	W.K. Boyd R.K. Jeffrey	Yes

MISCELLANEOUS

Conference Proceedings	Proceedings North American Fuel Technology Conference Ottawa, Canada. June 1-3, 1970. Cheques should be made payable to Secretary, North American Fuel Technology Conference, 555 Booth Street, Ottawa K1A 0G1, Ontario	collection of 17 papers	Price $16.00

1970 PUBLICATIONS OF THE CANADIAN COMBUSTION RESEARCH LABORATORY

Number	Title	Author	Released for Distribution
FRC 70/5 CCRL	SO_2 Concentrations in Flue Gas From Two High-Sulphur Canadian Coals - (an evaluation of earlier research data)	G.K. Lee F.D. Friedrich E.R. Mitchell	Limited Distribution
FRC 70/11 CCRL	A Proposal to Study the Effect of Radial Velocity on Turbulent Mixing Processes as Applied to Combustion - Presented to a Graduate Seminar, Queen's University, Kingston, Ontario, February 26, 1969	F.D. Friedrich	Limited Distribution
FRC 70/18 CCRL	Inhibition of Sulphuric-Acid Corrosion by Water-Base Points	G.K. Lee R.K. Jeffrey	Patent Description
Mines Branch Information Circular IC 211	Air Pollution: Causes and Control - La Pollution Atmospherique, ses Causes et sa réduction	H. Whaley F.D. Friedrich G.K. Lee E.R. Mitchell	Yes
FRC 70/35 CCRL	Air Pollution in Canada from Fuel Combustion - 1st Addendum to Mines Branch IC 211 - (Air Pollution Computations for OECD Joint Group on Air Pollution from Fuel Combustion)	F.D. Friedrich E.R. Mitchell	Limited Distribution
FRC 70/38 CCRL	An Automated System for Continuous Monitoring of SO_2, NO_2, and NO_x in Boiler Flue Gas	R.K. Jeffrey G.K. Lee	Mines Branch TB 131
FRC 70/49 CCRL	Boiler Performance Tests at Tunney's Pasture, Ottawa	R.G. Fouhse B.C. Post D.G. Savignac	Limited Distribution
FRC 70/56 CCRL	Boiler Performance Tests, Stoney Mountain Penitentiary, Winnipeg, Manitoba, March 16-20, 1970	R.G. Fouhse B.C. Post	Limited Distribution
FRC 70/59 CCRL	Boiler Performance Tests, National Defence Medical Centre, Ottawa, March 4-15, 1970	R.G. Fouhse	Limited Distribution

FRC 70/60 CCRL	Performance Tests, High Temperature Hot Water Generators, Central Experimental Farm, Ottawa, April 8-10, 1970	R.G. Fouhse B.C. Post	Limited Distribution
FRC 70/61 CCRL	The Dispersion of Multiple Plumes from a Large Thermal Generating Station	H. Whaley L. Shenfeld G.K. Lee M.S. Hirt S.G. Djurfors	To be Released in 1971
Mines Branch Research Report R 225	The Thermal Destruction of DDT in an Oil Carrier, April 1970	H. Whaley G.K. Lee R.K. Jeffrey E.R. Mitchell	Yes
FRC 70/55 CCRL	Characterizing Pollutant Emissions from Flames - Presented to the CGA National Technical Conference, Toronto, November 18-20 1970	F.D. Friedrich G.K. Lee E.R. Mitchell H. Whaley	Yes
FRC 70/76 CCRL	An Assessment of the Combustion Performance of Western Canadian Crude Oil - Preliminary Report	G.K. Lee F.D. Friedrich E.R. Mitchell	Industrial Confidential

1969 PUBLICATIONS OF THE CANADIAN COMBUSTION RESEARCH LABORATORY

Number	Title	Author(s)	Released for Publication
FRC 69/3 CCRL	Boiler Acceptance Test Coal Burning, High Temperature Water Generator. FRC, Corkstown Road Development, Ottawa, January 1969	E.R. Mitchell B.C. Post	Limited Distribution
FRC 69/23 CCRL	Slag Control in a Kraft Recovery Unit	G.K. Lee E.R. Mitchell	Industrial Confidential
FRC 69/55 CCRL	Boiler Performance Tests, St. Vincent de Paul Penitentiary, January 6-9, 1969	R.G. Fouhse B.C. Post D.G. Savignac	Limited Distribution
FRC 69/56 CCRL	Boiler Performance Tests, Ste. Anne des Plaines Penitentiary, January 13-17, 1969	R.G. Fouhse D.G. Savignac	Limited Distribution
Mines Branch RS 79	Control of SO_3 in Low-Pressure Heating Boilers by an Additive	G.K. Lee F.D. Friedrich E.R. Mitchell	J. Inst. F. Feb. 1969
FRC 69/66 CCRL	An Automated System for Continuous Monitoring of CO_2, CO and O_2 in Boiler Flue Gas	R.K. Jeffrey G.K. Lee	Mines Branch TB 115
FRC 69/82 CCRL	Sample Preparation and Analysis of Particulate Products of Combustion	R.K. Jeffrey	Limited Distribution
Mines Branch IC 219	Some Comments on the Interpretation of Response Surfaces	F.D. Friedrich	Yes
Mines Branch R 208	Combustion and Fouling Characteristics of Two Canadian Lignites	F.D. Friedrich G.K. Lee E.R. Mitchell	Yes
Mines Branch RS 80	A Proposed Canadian Standard for Estimating Atmospheric Dispersion of Combustion Source Pollution from Chimneys	H. Whaley	Atmospheric Environment, Pergamon Press, Vol 3, p 177-195, 1969
Mines Branch RS 92	Control of Oil Ash Deposits and Pollution Abatement by an Additive	G.K. Lee	Fuel Society J. Vol 23, 1969, Sheffield University.

3.10 - NEW HYDRO-METALLURGICAL PROCESSESS

by

H. H. McCreedy

This contribution to the Seminar covers the work of both the Hydrometallurgy and Chemical Analysis Sections of the Extraction Metallurgy Division. Our environmental control work, rather than being a series of isolated projects grouped under the heading of "Environmental Improvement" is instead an important consideration in most of our process development studies.

In one project we are concerned with the percolation leaching of broken uranium ore in underground workings with bacterially-active acid-sulphate solutions. The environmental aspects of this technique are as follows. The amount of acid needed for leaching some types of ore is reduced, the total volume of leach liquor per ton of ore required is greatly reduced, the process lends itself to solution recycle, and the amount of solid waste that has to be impounded on surface is reduced to about one third of that of a conventional leach plant. Sixty-two per cent of the uranium was dissolved in the mine test in 24 weeks, and eighty-three per cent was dissolved during a two year pilot plant test.

Techniques are already known for recovering the uranium and thorium from this type of solution.

In another project we are studying the feasibility of pressure-leaching relatively low-grade bulk flotation concentrates of sulphide minerals. To date we have been concerned with copper-nickel sulphide concentrates. This hydrometallurgical approach eliminates the SO_2 air pollution associated with roasting and smelting operations, although it has associated with it a soluble sulphate problem. Previous to this year it was found necessary to use 400 psi oxygen pressure to obtain copper extractions of over 90%. By regrinding the flotation concentrates to -325 mesh it has

been possible to get 95% of the copper dissolved from chalcopyrite, and 95% of the nickel from the associated pentlandite, in 6 hours contact time at only 80 psig oxygen and 110°C. The copper and nickel are recovered from solution by cementation with iron powder.

One of our studies this year in the application of the resin ion-exchange process for the recovery of soluble values, has been the construction of a multi-stage, fluidized-bed, IX absorption column in circuit with a moving, packed-bed regeneration column and a fluidized-bed washing column. This equipment will be used to demonstrate that ion exchange can be used to recover soluble metal from waste mine or mill solutions which contain some solid material.

One objective of our solvent extraction program is to apply solvent-in-pulp methods using a sieve-plate pulse column to the treatment of uranium-bearing leach pulps. If a successful SIP process was developed it would mean that the current liquid-solid separation and washing steps could be eliminated, thus reducing the volume of process solution that would require neutralization before disposal. The effects of some of the parameters on solvent losses have been investigated.

Our Chemical Analysis Section has been investigating the removal of trace amounts of arsenic by co-precipitation with the hydroxides, phosphates and carbonates of iron, calcium and magnesium. This is of significance in the treatment of effluents from mining operations where arsenic-bearing minerals occur.

REFERENCES

EMA 70-7 Bacteria Based Processes for the Treatment of Low-Grade Uranium Ores by W. A. Gow et al.

IC 259 Construction and Operation of an Experimental Sieve-Plate Pulse Column for Solvent Extraction of Metals by G. M. Ritcey et al.

EMA 71-10 Solvent-in-Pulp Processing Using Sieve-Plate Pulse Column by G. M. Ritcey.

EMI 71-22 Proceedings of the Meeting of the Canadian Uranium Producers' Metallurgical Committee by H. W. Smith.

3.11 - CHLORINATION PROCESSES - PHASE EQUILIBRIUM STUDIES IN THE (Fe·Co·Ni)-S-Cl SYSTEMS

by

A.H. Webster

ABSTRACT

The commonly - used pyrometallurgical processes for smelting sulphide ores lead to the formation of large amounts of sulphur dioxide, which, if discharged to the atmosphere, constitutes a serious source of air pollution. Chlorination has been considered as an alternative method for treating sulphide concentrates. Among the difficulties encountered with chlorination processes is the formation of a liquid phase in the material being chlorinated. An investigation was undertaken, therefore, to examine the melting behaviour of some systems involving sulphides and chlorides.

It has been found that there was no effect on the melting points of the separate components when mixtures were formed between iron sulphides and $FeCl_2$, between nickel sulphides and $NiCl_2$, and between cobalt sulphides and $CoCl_2$. By contrast, in the Cu_2S-CuCl system eutectic melting occurs at 389°C, 40° below the melting point of CuCl. Ferric chloride was found to react with ferrous sulphide (FeS) to form $FeCl_2$ and a more sulphur-rich pyrrhotite ($Fe_{1-x}S$) or pyrite (FeS_2) depending on the FeS to $FeCl_3$ ratio.

INTRODUCTION

The usual pyrometallurgical treatment of sulphide ores leads to the formation of SO_2. To avoid emission of the SO_2 to the atmosphere, and the consequent pollution, the sulphur dioxide must be removed from the waste gas stream, or an alternative process must be used. Hydrometallurgical processes are an alternative that is being widely used and that is being intensively investigated. Another alternative would be chlorination of the sulphide concentrate, with the formation of metal chlorides. The metal values might be recovered by electrolysis, or the chlorides might be leached, followed by a separation procedure, such as ion exchange or solvent extraction, and recovery by electrolysis. Chlorine gas, sulphur monochloride, HCl gas and $FeCl_3$ have

...2

been tried or proposed as chlorinating agents. There are considerable problems associated with chlorination, including corrosion and the partial fusion of the charge during chlorination. The latter problem is particularly serious if a fluidized bed or rotary kiln is used for the chlorination. It was to this problem of fusion that the present investigation was directed.

Samples of mixtures of anhydrous chlorides and sulphides of Fe, Co, Ni and Cu, sealed in evacuated silica capsules, were examined by differential thermal analysis (DTA) to determine melting and freezing points. Selected samples were examined by powder X-ray diffraction after completion of the DTA in order to determine the phases present.

RESULTS

Iron sulphides - $FeCl_2$.

The melting point of $FeCl_2$ (682°C) was not lowered by more than 3 deg C by the presence of FeS, $Fe_{0.87}S$ (pyrrhotite), or FeS_2 (pyrite). The solubility of the iron sulphides in $FeCl_2$ is, therefore, small. X-ray diffraction showed no evidence of compound formation between pyrrhotite and $FeCl_2$.

FeS - $FeCl_3$.

Ferric chloride is reported to melt at 307°C and to boil at a temperature only a few degrees higher, 319°C. It was found, however, that $FeCl_3$ reacts with FeS to form a more sulphur-rich pyrrhotite or pyrite. During heating of FeS-$FeCl_3$ mixtures, an endothermic reaction was generally observed at about 300°C, corresponding to fusion of $FeCl_3$. However, samples with a relatively large percentage of FeS did not show a corresponding exothermic peak on cooling. X-ray diffraction examination of the mixture after DTA showed that $FeCl_2$ had been formed together with a more sulphur-rich iron sulphide.

Nickel Sulphides - $NiCl_2$.

Nickel chloride is reported to sublime at about 980°C, well below its melting point, which was determined as 1012°C. The melting behaviour of stoichiometric NiS, which does not melt congruently, was not changed by the presence of $NiCl_2$. The melting behaviour of a nickel-sulphur composition with 56.7 atomic % Ni also was not altered by the presence of $NiCl_2$. It can therefore be concluded that the solubility of $NiCl_2$ in molten nickel sulphide is small. X-ray diffraction showed no evidence of reaction between nickel sulphide and $NiCl_2$.

Cobalt Sulphides - $CoCl_2$.

The melting behaviour of stoichiometric CoS, which, like NiS, does not melt congruently, was not affected by the presence of $CoCl_2$. Conversely, the melting point of $CoCl_2$ (724°C) was not lowered by the presence of CoS or by the presence of a cobalt sulphide composition with 56 atomic % Co. There was no evidence from X-ray diffraction of a reaction between the material with the CoS composition and $CoCl_2$.

Cu_2S - CuCl.

It is reported in the literature that CuCl (melting point 430°C) and Cu_2S form a eutectic at 389°C. Also, eutectic temperatures well below the melting point of the chloride have been reported for the systems AgCl-Ag_2S and $PbCl_2$-PbS, in marked contrast to the observed behaviour for the Fe, Ni and Co sulphide-dichloride systems. A study of the CuCl-Cu_2S system was undertaken, by the method used in the present investigation, and it was found that there is indeed a eutectic at 389°C. The apparent composition of the eutectic found in the present investigation was slightly higher in CuCl than the composition reported previously.

DISCUSSION

In the temperature range up to 600°C, the only liquid phase found to occur in the sulphide-chloride systems for Fe, Ni and Co was $FeCl_3$. Ferric chloride, however, will react with pyrrhotite, is easily hydrolysed, and is very volatile, boiling about 12° above its melting point. During chlorination with Cl_2 gas, the formation of $FeCl_3$ would be expected with excess chlorine. Also expected during chlorination with Cl_2 are elemental sulphur (boiling point 444.6°C) and/or sulphur monochloride (boiling point 138°C), depending on the temperature at which the chlorination is conducted. In the systems CuCl-Cu_2S, $PbCl_2$-PbS and AgCl-Ag_2S there are eutectics reported at the temperatures 389°C, 453°C and 375°C, respectively, so that liquid phases might be expected during chlorination of sulphide concentrates with significant amounts of these metals in the form of sulphides.

3.12 Reduction of Toxic Dusts From Pyrometallurgical Processes

by

G.E. Viens

Abstract

The Pyrometallurgical Group has several projects in progress that have as their objectives the abatement of pollution from pyrometallurgical operations. Extensive discussions with industry have been a continuing feature of this program. It is believed that the abatement of pollution in the near future can best be achieved by the addition of dust collectors to existing plants but in the longer term these projects or ones like them should contribute to the development of processes which should make possible pollution abatement without increasing processing costs.

Reduction of Toxic Dusts from Pyrometallurgical Processes

Many of the current projects in the Pyrometallurgical Group could be included under the above heading. The approach used has been to search for process modifications which would prevent the production of fume, or else retain the fumes within the process, rather than relying on the more classical approach of adding a dust collector to an existing process.

The second objective in many of these projects is to minimize the energy requirements of the process. In some cases these two objectives are interrelated in that energy is required to reduce the mineral to a lower state of oxidation before it becomes volatile and it is the escape of volatile metal or compounds which on exposure to the atmosphere becomes fume or dust.

To date the major part of our effort has been concerned with submerged arc furnace operation and we have had rather close liaison with several Canadian industrial firms for this work. During this liaison we have visited industrial production plants and laboratories, and in addition, technical staff from industry have visited our laboratories. In general it appears that in most cases, the short-term solution of pollution problems will be the addition of pollution abatement equipment to existing processes with only minor alterations to the process. In the longer term however there are several promising avenues for research and development which should make possible effective pollution abatement without increasing the processing costs.

With regard to laboratory work within the pyrometallurgy group, four projects deserve specific mention.

1) Experimental work to obtain data that will be useful for optimizing the size consist of submerged arc furnace materials. One of the causes of fume emission from submerged arc furnaces is a build up of gas pressure in the arc zone because the overlying bed of charge materials has become more or less impervious to the escape of this gas through it. When the pressure of this gas, usually laden with metallic vapours, becomes sufficiently high it violently erupts from the hot arc zone. Improvements in sizing of the charge materials should greatly diminish this problem. Pressure drop or permeability studies on a number of closely sized ore fractions as well as mixtures of sizes indicate that the permeability is increased both by using coarser sized material and by closer sizing. In the context of present furnace practice the close sizing is probably the factor which will yield the bigger improvement. Current furnace charges sometimes contain material 4" in diameter but they also contain materials of various sizes all the way down to about 1/8" in diameter. Currently a correlation between the laboratory data on carefully sized materials and data to be obtained from commercial charge mixtures is being attempted.

2) The electric smelting of iron ore to produce pig iron and the smelting of manganese ores to produce manganese alloys received attention during our discussions with industry. Because of the similarity between iron and manganese the possibility of utilizing a combined shaft electric furnace such as the one developed here by the pyrometallurgy group or the one developed in Japan was examined as

a means of minimizing pollution. The Japanese furnace has been developed to a commercial sized unit for manganese ores and has proven to be an efficient unit to minimize pollution. The major difference between it and our development lies in the shaft operation. In their unit they only extract the sensible heat from the arc furnace gases whereas the shaft-electric furnace that was developed here recovers both the sensible heat and latent energy from arc-furnace off-gas in the shaft furnace. We understand that the major disadvantage of the Japanese unit is that the increased efficiency realized by utilizing only the sensible heat of the off-gases is not sufficient to make it economically attractive. The Mines Branch unit is more difficult to assess because it has not been proven on a commercial scale.

3) The smelting of silicon metal has also received considerable attention. In this case, discussions with industry, observations of production units, literature surveys, thermodynamic and heat-balance calculations, as well as small scale experimentation in these laboratories, indicate that the chemistry involved in making silicon is very complex, and that vast improvements in the existing process should be possible. For example the current furnace practice permits the escape of about 35% of the original SiO_2 feed as fume. The largest part of this probably escapes as SiO gas which oxidizes to SiO_2 on contact with the atmosphere creating a very severe fume problem. In addition to generating a pollution problem, which can be solved by expensive dust collecting equipment, the escape of this

SiO represents a sizable energy loss from the system. The study of this system is continuing.

4) One final pollution problem which has received considerable attention by the Pyrometallurgy Group during the past year concerns the "fly ash" which is a residue from the extraction of petroleum products from the Athabasca tar sands. As exploration of tar sands advances large quantities of this fine fly ash are going to accumulate. It is so fine that it can be blown about by the wind. This problem is being studied in close co-operation with a prominent Canadian consulting firm. The present status is that two possible pyrometallurgical flowsheets have been developed in these laboratories to recover both Ni and V from this material. Sufficient laboratory work has been completed to confirm that both these flowsheets are probably technically feasible. The next stage will consist of economic evaluations on pilot plant operation. This project was greatly advanced near the end of 1971 by a co-operative sub-project with the Mineral Processing Division which resulted in a flotation method of separating the carbon in this fly ash from the metallic values.

3.12.1 COAL CARBONIZATION AND RELATED STUDIES

by

J.C. Botham*

ABSTRACT

Since the previous Mines Branch Seminar on Environmental Improvement the Metals Reduction and Energy Centre (MREC) has participated to a limited degree in studies directly oriented towards the alleviation of the pollution aspects of coal carbonization and its associated coal processing. Progress in this area is mainly restricted by the dissimilarity between commercial and experimental equipment. However studies, which are indirectly related to pollution control, are in progress and include innovations to conventional coke-making in slot-type coke ovens and to the development of new methods of coke manufacture. In this regard, the Canadian Carbonization Research Association recommended that MREC assign priority status to investigations dealing with pre-heating of coke oven charges, form-coking and dry-quenching of coke.

It should be pointed out that major renovations to Building No. 2, Mines Branch Research Centres, are presently in progress and the modifications will ultimately extend the scope of MREC activities in this field.

---

*Head, Metallurgical Fuel Engineering Group, Metals Reduction and Energy Centre, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

POLLUTION ABATEMENT IN THE COKE-MAKING INDUSTRY AND MINES BRANCH PARTICIPATION

As pointed out by MREC at a previous seminar the manufacture of coke by conventional means is generally recognized as a major contributor to air pollution. Ninety-eight percent of the coke produced in the United States originates from slot-type ovens. Ovens of this type represent a large industrial capital outlay and since they have a useful life of 20-30 years it is unlikely that a new process will completely displace conventional coke-making for many years. For example, in the United States there are about 250 batteries of ovens carbonizing about 80×10^6 tons of coal per year. These ovens still have many remaining years of service. The industry has recognized this situation and in the United States the American Iron and Steel Institute (AISI) and the Environmental Protective Agency (EPA) have a joint research program underway to develop ways and means of controlling pollution from existing conventional coke plants. In general, the most serious sources of air pollution occur during charging of the coal, pushing of the coke and quenching of the coke. It has been estimated that these emissions occur in the ratio of 60:30:10. The AISI-EPA combination have designed new equipment for coal and coke handling and have made modifications to oven ancillaries to alleviate the problem of air pollution. Their prototype system has been installed in the coke ovens of the Pittsburgh works of Jones and Laughlin Steel Corporation. The program is now in its second year and the system when tried and proven will be offered to the operators of coke oven batteries in North America. It is doubtful that MREC could contribute to this type of pollution control.

Preheating of coal prior to charging into the coke oven is of current interest to the industry on this continent and abroad. The advantages of this technique include increased productivity, use of poorer quality coals and improved coke quality. One process licensed by Coaltek Associates, Morristown, N.J., employs pipeline charging of the coke ovens and it has been claimed to reduce smoke and gases from coke ovens by as much as 70 percent. A Canadian

steel plant plans to adopt this technique to one battery of their coke plant. Initial preheated coal trials using their specific coal blend and pipeline charging were carried out at the Allied Chemical Corporation plant in Ironton, Ohio. MREC participated in the tests including pilot plant support studies.

The discharge of coke from the oven followed by quenching (normally with water) represents only 10 percent of the pollution of the total operation. The extent of air pollution at this stage of the coking cycle is related to the efficiency of the plant and the degree of final carbonization. For this reason, a Canadian steel plant intends to deliberately soak their coke, with an accruing loss in productivity, to ensure that no green coke occurs during their pushes. Dry quenching of coke has gained prominence in the U.S.S.R. A recent article indicated several existing plants using this method and stated that the new batteries of tall ovens (7 m) would be equipped with dry cooling units. Dry quenching of coke has the advantages of improved coke quality and a thermal saving in the blast furnace. In addition it prevents the discharge of gas and fumes when the coke is pushed (i.e. smokeless pushing). One of the Canadian steel plants has expressed an interest in studying the feasibility of adopting this method of coke quenching. MREC has two dry quenching units for use in carbonization studies with the 18-inch and 12-inch movable-wall coke ovens.

From the longer term point of view, the steel industry in general has under consideration the ultimate use of a substitute for conventional metallurgical coke. Processes, which produce a form-coke appear to be the form of carbon likely to supplant the slot-oven coke. Many advantages are attributed to form-coking including a continuous process with a better control of the polluting aspects of carbonization. There are many processes of this type. On this continent the FMC process and the Consolidation Coal Company process are probably in the fore-front while in Europe the BBF, HBNPC and the Simon Carves processes are of prime interest. Although form-coking techniques have many attractive features, at this point in time, there is no conclusive evidence concerning their comparative performance with conventional coke in the iron blast furnace. MREC currently has in progress several projects

associated with form-coking. Initial studies are at the laboratory-scale but pilot plant investigations are contemplated.

MREC PROJECTS RELATED TO POLLUTION ABATEMENT

Coal Suppression During Unit Train Transportation (T.A. Lloyd)

The loss of airborne fine coal during transportation from mine to tidewater is of particular concern to those companies in Western Canada mining coking coal for the export market. Studies have been carried out specifically for Kaiser Resources Limited. The relative efficiencies of various suppressant reagents have been demonstrated under simulated wind conditions. As a result of this initial study, investigations for other companies were made in relation to the use of similar suppressants to reduce dust losses from stockpiled coal.

Preheated Coke Oven Charges (W. Gardiner and J.G. Jorgensen)

The use of preheated coal in coke-making is a continuing MREC project. The Algoma Steel Corporation Limited have under serious consideration the application of preheated coal to one of their new coke oven batteries. The pipeline method of charging will be used. During August 1971 MREC participated in commercial scale trials at the Allied Chemical plant at Ironton, Ohio. Support studies including technical-scale coke oven tests were carried out in Ottawa.

As a follow-up to earlier studies MREC intends to continue investigating the advantages of carbonizing agglomerated coal charges (hot and cold) in slot-type ovens.

Form-Coking Studies (Dr. B.J.P. Whalley and Dr. D.A. Reeve)

Studies on form-coking to date have been confined to the development of facilities to, (1) examine the time-temperature-pressure mechanisms of the various form-coking processes, (2) manufacture form-cokes under conditions simulating the various processes, and (3) assess the quality of form-cokes, particular in relation to their use in the blast furnace.

Form-cokes produced from various processes have been examined and compared with conventional cokes.

Arrangements have been made through the Canadian Carbonization Research Association to send samples of coal to Europe for form-coking studies by the BBF process (Bergbau-Forschung). Samples of the form-cokes produced will be returned to Canada for MREC evaluation.

The modifications to Building No. 2, Mines Branch Research Centres, presently underway, will provide the space and services for expanding the form-coking studies to the pilot plant scale.

Tar Recovery System for Technical-Scale Coke Ovens (E.W. Montgomery)

A tar recovery system has been designed and adapted to one of the 12-inch movable-wall coke ovens. Ultimately similar units will be used on the other experimental ovens. The apparatus will permit the collection of a representative tar sample for subsequent analysis. The evaluation of the tar quality will assist in assessing the feasibility of preheated coal charges and other conditions of carbonization related to reduced air pollution.

Dry Quenching of Coke (Dr. D.A. Reeve, W. Gardiner, P.C. Lorince)

Two dry quenching towers have been designed and constructed for use with the 12-inch and 18-inch movable-wall coke ovens. Studies will be carried out to show the advantages of this technique over the conventional wet method.

JCB/cm

RELEVANT PUBLICATIONS

1. Plaks, Norman, "Improved Processing Methods to Control Air Pollution Emissions from Cokeries", Seminar on Air and Water Pollution Arising in the Iron and Steel Industry, Economic Commission for Europe, Steel Committee, Leningrad, August 23-28, 1971.

2. "Test Facility on J & L's Coke Ovens", Skillings' Mining Review, Vol. 60, No. 9, February 27, 1971.

3. "A Cost Analysis of Air-Polluting Controls in the Integrated Iron and Steel Industry" Contract No. PH 22-68-65, Battelle Memorial Institute, May 15, 1969.

3.12.2 UTILIZATION OF DISCARDED AUTOMOBILE TIRES IN COKE-MAKING OPERATIONS

by

W.R. Leeder*

ABSTRACT

Initial investigation was made of the possibility of using discarded rubber tires as a source of carbon in slot-oven coke making or as binder in form-coke making.

Tires represent one of the most unique and troublesome materials with which our automobile-oriented society must contend. In particular, cities such as Vancouver have even considered tying them in large bundles and dropping them in the ocean. One possible use of this material which is presently being considered is the conversion of tires into coke. Since most of the material is carbon black or carbonaceous material shredded tires could probably be incorporated into slot-oven or into form-coke. Its use in this capacity would probably be that of binder. Current work is being aimed at using it as a binder in hot briquetting of coal and for addition to oven cokes charges [1]. The idea of tire utilization was stimulated by a request for assistance by Pioneer Ventures Company Limited of Vancouver, a company which amongst other things is involved in industrial dump utilization and management.

REFERENCE

12. Leeder. W.R. (1972), "Utilization of Discarded Automobile Tires in Coking Processes" (pending).

---

*Research Scientist, Special Studies Group, Metals Reduction and Energy Centre, Dept. of Energy, Mines and Resources, Ottawa, Canada.

3.12.3 - NEW METALLURGICAL AND COAL BENEFICIATION PROCESSES

by

John H. Walsh

As other officers of the Metals Reduction and Energy Centre have dealt with projects within their respective spheres of responsibility this section will be confined to reporting on environmental improvements not otherwise given.

A.) OXYGEN STEEL MAKING

A new bottom-flow steelmaking process (known as the Q-BOP in the United States) is now reaching industrial maturity. The present annual capacity of steel processed by this new technique now exceeds 6 million tons and it is expected that in the near future production will reach 10 million tons annually. This new process is noted here because although the rights are held by the German firm that perfected the process, the original concept was Canadian and, in fact, some of the earliest work on this process was conducted in the Mines Branch laboratories. It is well known that oxygen steelmaking processes give rise to a fine iron oxide dust that leads to serious air pollution hazards; this difficulty is overcome by elaborate dust collection techniques which are costly in both capital and operating charges, especially when it is realized that the gases leaving the process are about 1600°C and are still largely uncombusted. The new process is believed to give rise to somewhat less dust production than the traditional top-blown method. The heart of the technique is the use of oxygen at sufficiently high pressure that some Joule-Thomson cooling is achieved together with a shroud of propane gas, which under these conditions acts as a coolant relative to the combustion of the oxygen with the carbon of the liquid iron, so that, taken together, the two cooling actions give a reasonable degree of protection to the refractories used in the furnace bottom.

One of the techniques for recovering dust from the exit gas of the conventional oxygen steelmaking process leads to the presence of this finely divided (5 micron) dust in the cleansing water. This poses serious difficulties in the final water clarification procedures used in the water treatment circuit. Dr. H.A. Hamza, NRC Postdoctoral Fellow working at the Western Regional Laboratory under the direction of Dr. Jan Visman, has conducted studies of the application of long-chain flocculants to the problem of this flue dust recovery. It has been found with the use of a suitable quantity of reagent, that flocs of sufficient strength can be formed which will withstand subsequent cyclone separation techniques. The removal of a substantial

part of the fine flue dust in the water by such a combination of flocculation and cycloning reduces the load on subsequent down-stream water clarification equipment appreciably. Some interest has been expressed industrially in this application and a design of a small plant is proceeding.

It may be that this combination of processes will find general application in the water clarification field and even in certain leaching processes where the removal of very fine ferric hydroxide continues to be a very serious impediment. Work is continuing in Edmonton on this technique.

B.) REMOVAL OF PYRITE FROM HIGH SULPHUR COALS

Where practicable, it is desirable to remove pyrite from coal prior to its use either in combustion or in other industrial applications. Where coal is to be used dry, such as in intermediate stages of the hot-charging of coking coals to coke ovens, there is the possibility of the application of electrostatic processes and this type of separation is being carried out at the University of Western Ontario with some financial support of the Department (5). Where coal must be handled wet, the ultimate method follows the lines of the NRC "spherical agglomeration process" where all the coal can be ground very fine (to say 60% or more minus 325 mesh), and then the carbon-bearing constituents separated by the addition of oil which causes agglomeration to a large enough size to allow their effective separation by several different means. In the case of the Mines Branch process (which is now known as the EMR Process - Technical Bulletins 141 and 142) the technique is really a staged separation whereby the coal is cycloned to achieve gravity rejection of as much pyrite as possible with the coal being stage-ground if required to free more pyrite, which is then separated again in a subsequent cycloning step which is, in turn, followed by an oil agglomeration treatment of the fine coal. This last step has the twin objective of allowing the separation of still more pyrite and of obviating the need for thermal drying. Studies have been made in the last few months of samples of coal from Cape Breton to determine optimum separation possibilities. An industrial design has been prepared based on these studies and a formal plan for an industrial-scale developmental plant has been made by a contractor to the Cape Breton Development Corporation.

C.) UPGRADING LOW SULPHUR COALS

Substantial reserves of low-sulphur coal occur in the lignite fields of Southern Sakatchewan. In normal combustion practice, this coal is mined and used, if not nearby, within a fairly close range of the lignite fields in boilers especially equipped to handle these low-rank coals. These coals are characterized by a very high moisture content, which is reflected in their low energy content, and a high sodium content, which is reflected in their generally low ash softening temperature. Studies aimed at using these coals in steam plants designed for higher rank coals located a great

distance from the lignite fields indicated a need for methods of increasing the energy content of the coal to allow more economic shipment and more suitable combustion characteristics, and also lower sodium content to prevent excessive fouling of the tubes of the steam plants. Work to date has been based on a technique of combining physical and chemical treatment of the lignite whereby about one-half of the original sodium can be rejected to the process water. This is achieved by the presence of a suitable quantity of calcium chloride in the process water which acts as ion exchange agent to react with sodium bound in the coal. After processing, the coal can be dried and prepared for shipment by pelletizing with oil additions to overcome spontaneous combustion. Many difficulties lie in the way of the development of a satisfactory process to achieve these ends but efforts have proceeded to the point where a Canadian patent application had been filed to cover the early process stages. The main goals are to use more Canadian coals in thermal generating plants and to decrease the amount of sulphur dioxide produced per ton of coal burned.

D.) ABATEMENT OF POLLUTION IN IRON AND STEEL PRODUCTION

Because of the difficulties with certain iron-and steelmaking processes with respect to pollution problems, industrial attention has been focused on the possible use of very large induction furnaces for the steelmaking field. Small induction furnaces have long been used to make small quantities of steel in experimental or very special categories and induction furnaces have been used for some time in the iron foundry industry, in part to displace cupolas. Because of the possibilities inherent in the further development of this kind of unit, especially when the possible melting of sponge iron is taken into account, an industrial consultant was retained by the Centre to prepare a thorough report on this interesting process when operating on standard electrical line frequencies (60 cycles). This work has been reported in Information Circular 278 (4).

REFERENCES

1.) Technical Bulletin 141 "Coal Washery Design - I, the E.M.R. Process", by J. Visman. Div. Report MREC 71/72 WRL, EMR, September 1971.

2.) Technical Bulletin 142 "Coal Washery Design - II, The Computation of Recirculating Loads", by J.L. Picard. Div. Report MREC 71/73, WRL, EMR, June 1971.

3.) H.A. Hamza and J. Visman "Application of Flocculants in Hydrocyclone Separation", to be presented to the Annual General Meeting of the Canadian Institute of Mining and Metallurgy, Ottawa, Ont. April 10-12, 1972.

4.) Information Circular 278 "Application in the Steel Industry of Large Line-Frequency Induction Furnaces", by J.E. Rehder, Div. Report MREC 71/66, EMR, October 1971.

5.) "Pyrite and Gangue Removal from Canadian Coals by Means of Fluidized Beds and Electric Fields", by I.I. Inculet, M.A. Bergougnou, and John Harris, to be presented at the Annual General Meeting of the Canadian Institute of Mining and Metallurgy, Ottawa, Ont. April 10-12, 1972.

3.13 RE-USE OF MINERAL WASTES

by

R. K. Collings*

SUMMARY

The activity within the Mineral Processing Division relative to the re-use of mineral wastes is in two parts -

1. Research towards the recovery and conversion of waste mineral materials to useful products, and
2. The re-use of waste water in mineral separation processes.

The materials of prime initial concern in Sub-Activity 1 (above) are the solid mineral wastes from mining, processing, chemical and metallurgical plants that appear, on the basis of composition, tonnage, location, etc., to have potential as substitutes for natural minerals in which Canada is, or may one day become, deficient and which often therefore must be imported, or produced in Canada at relatively high cost. The program assumes a six-point approach to mineral wastes as follows -

1. Inventory of wastes.
2. Selection of wastes for research projects.
3. Examination, including mineralogy, and chemical and physical characterization.
4. Beneficiation and conversion.
5. Process and/or product evaluation.
6. Utilization.

---

*Head, Non-Metallic and Waste Minerals Section, Mineral Processing Division.

The mineral waste projects that were active in 1971 in the Division were as follows -

1. Mineral waste inventory.
2. Phospho-gypsum for gypsum products.
3. Uranium tailings for glass.
4. Magnesium residues for cement.
5. Barite tailings for drilling mud.
6. Mineral wastes in concrete.

These projects are briefly described under "Progress 1971" (attached).

Owing to a lack of staff, no laboratory progress was made in the area of the re-use of waste water in mineral separation processes. Additional funds and increase in establishment are necessary in order to advance this project.

PROGRESS IN 1971

1. Mineral Waste Inventory

A province-by-province inventory of mineral wastes from mining and mineral processing, metallurgical, and chemical plants, is being made. When completed, this inventory will serve as a basis for the selection of projects for laboratory research. The inventory for the Atlantic Provinces is well in hand and a report on this section will be complete in another month or so.

2. Phospho-Gypsum for Gypsum Products

Laboratory investigation of waste gypsum residues from phosphate fertilizer plants for gypsum products manufacture has been a continuing project over the past 7 or 8 years. The residues investigated were from the following plants -

1. Sherritt Gordon Mines,
   Fort Saskatchewan, Alta.

2. Imperial Oil Ltd.,
   Redwater, Alta.

3. Electric Reduction Company,
   Port Maitland, Ont.

4. St. Lawrence Fertilizer,
   Valleyfield, Que.

These were selected for study because they were near to gypsum products plants that obtained their requirements of natural gypsum from distance source. The results of this research were promising and industry has indicated considerable interest in this project. The work is reported on in five investigation reports, and a paper summarizing the results of this work has been prepared for presentation at the Annual Meeting of the Canadian Institute of Mining which will be held in Ottawa in April.

3. Uranium Tailings for Glass

Concern over future sources of raw materials for glass manufacture has been expressed by at least one major Canadian glass company. In the past, the Canadian glass industry has used only top-quality silica sand in the glass batch;

however, it now appears that lower-purity sand may be acceptable. High-quartz tailings, such as those from the uranium mines of the Elliot Lake area, presumably would have some potential as glass batch raw material. With this in mind, a sample of tailings from Rio Algom's mine was investigated. Results of a preliminary study of one small sample were not particularly interesting. While some improvement in quality was achieved by water washing and magnetic separation, the resulting product did not meet current glass sand specifications.

	Beneficiated Product	Current Specifications
SiO_2	87.5 %	99.0 %+
Fe_2O_3	0.8 %	0.04%
Al_2O_3	4.9 %	0.50%
CaO+MgO	0.12%	0.15%
K_2O	3.4 %	-
L.O.I.	1.9 %	-

Further work is planned on larger and more representative samples.

4. Magnesium Residues for Cement

Samples of waste residues from a plant producing magnesium by the vacuum distillation process at Haley's Station, Ontario, were investigated as possible source material for cement manufacture. The material is essentially a lime-silicate mixture (CaO - 60%, SiO_2 - 35%). Results to date have not been very promising; however, some further work is planned.

5. Barite Tailings for Drilling Mud

Work on the recovery of barite from a zinc mine tailings in Newfoundland for use as oil-well drilling mud was completed during the early part of the year. A flotation product grading 92-93% $BaSO_4$, which is approximately drilling mud grade, was produced. The project was turned over to the Nova Scotia Technical College, Halifax, N.S., for investigation at a pilot plant level.

6. Mineral Wastes in Concrete

Structural parts of many industrial installations are often subjected to sustained or cyclic elevated temperatures. Conventional concrete, having little heat resistance, is not suitable for such applications. This project is concerned with the use of certain mineral wastes for improving the heat resisting properties of concrete.

In order to increase the heat resistance of concrete made with normal portland cement, two possibilities should be considered:

(1) The use of heat-resistant aggregates,

(2) The use of microfillers as thermal stabilizers of portland cement.

Two types of heat treated aggregates, expanded shale and slag, were used. The first is lightweight aggregate of the coated Haydite type producued by Domtar Construction Materials Ltd., at Mississauga, Ont. The other is blast furnace waste which is processed and marketed as pelletized granulated slag by the National Slag Company, Hamilton, Ont.

Fly ash, calcined shale dust, silica flour and wash-residue from slag cooling ponds were used as thermal cement stabilizers. To evaluate the potential of these materials, pozzolanic activity tests were carried out as a preliminary phase in this project. Mortar tests, chemical analyses, fineness determination, and water requirement tests, also were made.

Concrete mixes were made and cylinders and beam test specimens were moulded for fire exposure tests. A total of 329 test beams, 3½ x 4 x 15-in., and 467 test cylinders, 4 x 8 and 6 x 12-in., were prepared.

An elaborate firing programme has been designed with exposure temperatures up to 1000°C. After pre-conditioning of test specimens for about 3 months by air drying, they will be tested before and after heat exposure for changes in physical properties (ultrasonic pulse velocity measurements and final breaking tests).

BIBLIOGRAPHY

(1971)

1. Collings, R.K., Karpoff, D., Brown, G.A., "An Evaluation of Gypsum Residue from Valleyfield, Quebec, for Gypsum Products Manufacture", Mines Branch Investigation Report IR 71-9, 10 pp.

2. Collings, R.K., and Brown, G.A., "An Evaluation of Gypsum Residue from Port Maitland, Ontario, for Gypsum Products Manufacture", Mines Branch Investigation Report IR 71-10, 11 pp.

3. Collings, R.K., Bartley, C.M., Winer, A.A., Brady, J.G., "The Wastefulness of Waste", Mines Branch Report MPI(A) 71-27, 8 pp. Published in the Annual Review Number of The Northern Miner, November, 1971.

4. Collings, R.K., "Evaluation of Phospho-Gypsum for Gypsum Products Manufacture", Mines Branch Report MPI(O) 71-37, 24 pp. For presentation at the Annual Meeting of The Canadian Institute of Mining and Metallurgical Engineers, Ottawa, Ontario, April 1972.

3.14.1 ION EXCHANGE AND NEUTRALIZATION STUDIES FOR POLLUTION ABATEMENT OF ACID MINE DRAINAGE WATERS

by

A. J. Gilmore

ABSTRACT

The main objective of these studies was to treat contaminating mine waters and produce effluents of low metal concentrations tolerable to human and aquatic environments. Acidic mine waters, emanating from base metal mining operations, were treated by the application of ion exchange and neutralization technologies.

Lime neutralization of acid waters to high pH-levels produced effluents of very low base metal concentrations and high hardness. Ion exchange, with sulphonic acid resins, (1) produced effluents of tolerable base metal concentrations, and (2) will potentially recover valuable metals otherwise discharged to tailing areas by liming techniques.

INTRODUCTION

The application of neutralization and ion exchange technologies was examined, in 1971, for the pollution abatement of surface and sub-surface acid mine drainage (AMD) waters, from base-metal mining operations. Seasonal variations in the precipitation cause these drainage waters to vary widely in

(1) pH
(2) Flow rates
(3) Dissolved and suspended solids
(4) Soluble contaminants of base metals and iron.

The value of base metals, in some drainage waters is estimated to be in the $100,000 to $500,000 a year range.

In our studies, we have endeavoured to decrease the concentrations of these base metal contaminants to tolerable levels. However, these levels, (1) vary with the geographical location of a drainage problem under the jurisdiction of a water authority, and (2) may, or may not, be established by a water authority at the present time.

A. Copper and Zinc Recovery by Ion Exchange

An effluent of tolerable concentrations for each of Cu, Zn and Fe has been produced by a cation exchange-neutralization treatment of a simulated AMD water.

Following adsorption on a sulphonic acid exchanger, the base metals and iron were concentrated in a fraction of an acidified brine regenerant. A selective precipitation of this fraction, removed the iron to give a bulk product of about 50% Cu + Zn.

Concentrated brine regenerants were not discharged to the environment, but were fortified and recycled to subsequent regeneration cycles.

Liming of the barren effluent neutralized the acidity, and decreased metal concentrations to <0.1 ppm.

This ion exchange-neutralization application was shown to be chemically feasible, and capable of lowering metal concentrations to tolerable levels. Ion exchange, dependent

upon AMD volumes, concentration and the market value of metals recovered, is economically attractive compared to neutralization costs of acidic coal mine waters. The value of recoverable metals could, potentially, offset the cost of pollution control of a mining operation.

B. Nickel Recovery from a Waste Stream

A metallurgical-grade nickel product was produced by a similar ion-exchange treatment of a synthetic Sudbury mine water containing low concentrations of Ni, Cu and Fe. The effluent, from the sulphonic exchanger, was <20 ppb for each of the metals and should be suitable for mill recycle or discard to natural streams.

A product of about 50% Ni resulted from the selective precipitation of a fraction of the brine regenerant. Calcination increased the grade to about 77% Ni, with minor amounts of Cu and Fe. Again, gross concentrations of chloride would not be discharged to the environment, but would be recycled.

This study demonstrates the technological capability of producing a high-grade nickel product and, at the same time, removing very low concentrations of metal from mine water, to meet the acceptable levels of one provincial water authority. The nickel product, amounting to a small percentage of daily nickel production could be further purified at a Sudbury refinery. The recoverable nickel, by this proposal, has an estimated value of the order of $200,000 a year, based on published information.

C. A Comparison of Two Process Circuits

Two circuits, (1) ion exchange and (2) neutralization followed by ion exchange "polishing", have been compared to determine which circuit would produce the best attainable effluent concentrations. This work was performed on an acidic quarry water from an abandoned mine operation in New Brunswick. In this province, there is grave concern for the maintenance of trout and salmon life in areas of present and future base-metal mining operations.

Neutralization of the acidic quarry to pH 10.0 with CaO produced a filtrate of 4 and 19 ppb of Cu and Zn respectively, and 1600 ppm of hardness. "Polishing" of the filtrate, with a sulphonic exchanger, increase Cu concentration about 3 times and removed the hardness.

Direct application of the quarry water, to the sulphonic resin, gave an effluent of Cu and Zn concentrations, 5 to 7 times that of neutralization alone. Hardness was, again, almost eliminated.

In New Brunswick, very dilute concentrations of Cu and Zn in the presence of a degree of hardness are mandatory for the survival of aquatic life, according to Fisheries Service biologists. At the present time, these concentrations have not yet been established.

Lime neutralization of the acidic water would be an answer to this problem, due to the isolation of this abandoned quarry. The filtrate, if found suitable to the Fisheries Service authorities, could be discharged to the natural streams. The settled solids could be buried in the abandoned quarry, and the entire area then levelled and landscaped to forestall a reoccurrence of the problem.

DISCUSSION

Large volumes of AMD water can be treated by liming, to reduce base-metal contaminants, but large volumes of solids are created and discharged in disposal areas. Stoichiometrically, 1 Ton CaO produces 3 Tons gypsum ($CaSO_4.2H_2O$). Depending on TDS content of water treated, the weight of dewatered gypsum and metal hydroxides could be of the order of 2 to 3 times that of gypsum alone.

Lagoons of gelatinous, unsightly solid wastes occupy up to hundreds of acres of real estate. The question may be posed, "Have we traded water pollution for land pollution?" Other questions arise, (1) "What is solubility of these precipitated base metals in the lagoons, when exposed to a percolating leach of ground water or rainfall?", and (2) "Will vegetation, grown on these disposal areas, endanger bird and animal life?"

Recovering these valuable metals, at the outset, as a scavenging operation, would remove these metals from the water environment and put them to man's use. This view, gains some importance in an era of impoverished metal reserves, to fill the ever-increasing demands of an exploding population.

CONCLUSION

The technologies of neutralization and ion exchange may be applicable to numerous pollution abatement problems

under the jurisdiction of several water authorities. Lime neutralization of AMD waters to a high pH will produce effluents of very low base metal concentrations and high hardness.

Ion exchange, (1) produces effluents of tolerable base metal concentrations and low hardness, and (2) has the potential of recovering valuable metals otherwise lost to solids disposal areas by liming.

3.14.2 - AN EXPERIMENTAL STUDY OF THE WEATHERING OF MILL TAILINGS

by

A. Jongejan

ABSTRACT

A study of the variables involved in the weathering process of tailing ponds has been started in connection with investigations on water pollution.

The daily variation of the pH of water percolating and recirculating through a tailing sample from the Hudson Bay Mining Company was measured during tests of the design of percolators required for the experiments. The pH appeared to reach an equilibrium at approximately 8.25, whether acid or neutral water was used initially.

The daily variations of the pH, redox potential and conductivity of waters percolating through various samples of a tailing from the Heath Steele Mine in New Brunswick were measured, when the performance of a batch of twelve percolators was being checked.

The preliminary indication of the combined results was that the final pH of the waters apparently depended on the exposed grain surface area. The more the grain surface was exposed to water by dilution with sand, the more acid the water became and the more the Eh-pH equilibrium represented the oxidation of ferrous ions.

Although the determination of the daily variation of the chemical compositions of the waters is planned, no analytical results are available yet. In addition to the chemical aspects of the interaction between various minerals in the weathering process, the microbiological and physical aspects are also being investigated.

PROGRESS IN 1971

In the study of the effect of slagheaps and tailings on the pollution of water, which was listed in the report of the 2nd Mines Branch Seminar on Environmental Improvement, preference was given to problems concerning the weathering of mill tailings over problems associated with slag heaps. Although the variables in the weathering of slags would be more controllable, thus making the study of slags preferable from an experimental point of view, the effect on water pollution from tailing ponds would be expected to be more significant, as it has already been recognized as a major problem.

Because of the urgency to supply information on the variables involved in the weathering, the preliminary experiments needed to develop the most suitable methods and instrumentation were started using actual tailing samples, so that hopefully some indications about the process might be obtained.

The study is specifically concerned with the results of the interaction between various types of minerals and the composition of the water that percolates through the tailing in nature. For this purpose, a few different designs of existing percolators were tried out and modified to suit the requirements of the study. In these tests a tailing of the Hudson Bay Mining Company was used and the pH was measured daily.

Weathering is a lengthy process, so that experiments on the subject are very time consuming. The run on the Hudson Bay tailing lasted approximately 100 days, because the performance of the apparatus had to be based on runs possibly involving that length of time. In this run, in which 2 liter of distilled water percolated and recycled through 60 grams of tailing, the water was acidified to pH 4 with sulfuric acid. After about 30 days the pH settled at approximately 8.25. When pure distilled water was used, the same pH was reached after the water had been acid during the first few days.

One of the numerous variables in the problem is the fine grain size of the tailing, which retards percolation to a certain extent and produces

stratification in the sample. In order to get an idea about the most favourable rate of solution of the minerals as a function of the exposed surface area, tailing samples have been diluted with sand. Consequently, a sample of purified sand was also run in the first experiment. After reaching a pH of approximately 7.50, probably due to its ion-exchange properties, an equilibrium pH of 6.50 was reached.

In the second experiment, during which the performance of a group of twelve percolators was tested, a tailing sample from the Heath Steele Mine in New Brunswick was used. This tailing contained more sulfides than that of the Hudson Bay Mining Co. according to the chemical analysis. In addition to pH, redox potential and conductivity of the water were also measured daily. Since the instrumentation for the required daily analysis of low metal levels in small samples is not yet available, 10 relevant elements were analysed in a 50 ml sample during the run, in addition to the sample taken at the end of the run.

The details of the conditions in each percolator have been described in an Investigation Report, but a few of the indications concerning the weathering process will be mentioned. The starting pH of the water was adjusted to 4. The experiment lasted 75 days and the conductivity of the water was still increasing at the end of the run.

Although the waters percolating through 100-200 grams of tailing samples became basic (pH 7.5-7.7), those flowing through samples in which a greater surface area was exposed by mixing them with sand became acid after initially being basic. The water in a percolator in which iron sulfide was mixed with sand also remained acid. It is quite possible that the alkalinity of the water originates in the gangue minerals in the tailing, depending on the flowrate of the water and the exposed surface of the minerals. While the tailing contained only 1-2% of lime, the calcium content in the water at the end of the run was comparatively high.

The daily fluctuation in the pH in the Heath Steele tailing was larger than that in the Hudson Bay tailing, which again may originate in the greater content of iron sulfides in the Heath Steele tailing.

It is thus very possible that transient phenomena are of importance. This indication is in agreement with the procedure, used in practice, of allowing the effluents of the Heath Steele tailings to reach a state of equilibrium in several lagoons.

A few other phenomena were indicated during the second run. The results of the chemical analyses showed that although the contents of most elements in the water had gradually increased, others had decreased after an initial increase, possibly due to precipitation. Layering and a retarding effect on the flowrate could be observed. In view of the foregoing indications it appeared preferable to divide the project into two parts one focussed on the physical aspects of the problem, in other words the effect of layering, penetration, intermittent partial drying, etc., and the other dealing with the chemical effects of various mineral combinations on the water, including the microbiological aspects.

The sample of the Heath Steele tailing, as well as parts of the percolator, were sterilized before the start of the experiment. Two percolators were inoculated with a sample water from an acid creek on the tailing pond of a gold mine in Quebec, assuming that it would contain Thiobacilli. After progress had been made in the development of the required microbial methods, it appeared that this water contained mostly Ferrobacilli, which do not oxidize sulfur but derive their energy from the oxidation of ferrous salts. Tests during and after the run in which the microbial population appeared to decrease, may indicate that the microbial population is possibly specific for each tailing pond environment, not only concerning the spatial distribution of the population, but also its composition. It is thus possible that the study on the variables due to microorganisms has to be approached from the ecological point of view. A study of this possibility has been started and is being pursued as time permits, using samples collected from tailing ponds of fourteen different mining operations during the summer of 1971. During the field work it became evident that the number of variables possibly involved in the weathering process is very large. However, on the other hand, it is possible that the effects of water pollution

due to the seepage of tailing ponds are local. For instance, some evidence was obtained that Lac Pelletier acts as a kind of settling basin for the very acid tailing creek draining from the tailing ponds in the Noranda area, because the River Pelletier, which leaves the lake about one mile below the outlet of the tailing creek, appeared to have a pH of 7.4. Finally it should be emphasized that the possibilities mentioned before refer to one particular tailing and only one experiment. What is valid for one tailing may not be valid for another.

BIBLIOGRAPHY

A. Jongejan, "An Experimental Study of the Weathering of Mill Tailings in Collection with Water Pollution. Part I". Mines Branch Investigation Report IR 72-4.

3.14.3 ADSORPTION OF TRACE QUANTITIES OF METAL IONS BY CLAY MINERALS

by

H. F. Steger

ABSTRACT

From eight samples of Canadian bentonite previously obtained by the Mines Branch, Aquagel and Magcogel showed the greatest promise in preliminary tests. The ion exchange capacity of these bentonites was determined to be 32.5 and 25.8 meq/100 g for Aquagel and Magcogel respectively. Calcium is the predominant sorbed cation.

The ability of these bentonites to sorb trace metal ions in the presence of large excesses of sodium and calcium was studied, at first, in acetate medium. The amounts of trace metal ion sorbed by the clays depend both on the concentration and nature of the trace metal ion. The facility of sorption decreased in the order Fe(II) > Cu > Pb > Zn for Aquagel and Fe(II) > Pb > Cu > Zn for Magcogel.

A study in "thioacid" medium (i.e., sulfate and dithionate) is underway. Initial results show that bentonites may behave very similarly herein as compared to acetate medium.

INTRODUCTION

Before beginning, I should like to say that, for this discussion, clay minerals will mean the bentonite clays in which the active mineral is montmorillonite. The adsorption of trace quantities of metal ions by clay minerals is an ion-exchange process. Basically, clays have surplus negative charge in the lattice which is compensated for by cations adsorbed at the surfaces. The most common cations are calcium, sodium, magnesium and potassium. These adsorbed cations are, in general, exchangeable for others present in aqueous or alcoholic media. The adsorption of trace metal ions, therefore, requires their exchange from the solvent phase for the alkali and alkaline earth metal ions in the clay phase.

As the model of mine effluent, the discharge from the tailings pond system of a base metal mine in northeastern New Brunswick is used. This is basically a "thioacid" medium (i.e., sulfate, sulfite, thiosulfate and dithionate) in which the total sulfate concentration is ~1400 ppm. Na^{+} and Ca^{2+} are present at the 500 and 300 ppm level, respectively. The trace metal ions are Fe^{2+} and Zn^{2+} at ~2 ppm, Pb^{2+} at ~1 ppm and Cu^{2+} at ~0.02 ppm.

There are five main points of interest, or rather questions, to be considered in the use of bentonite clays in "thioacid" mine effluent.

(1) Alkaline earth metal ions are, in general, more strongly adsorbed than transition or heavy metal ions. Thus, how great will be the likelihood of bentonites to adsorb trace quantities of transition or heavy metal ions in the presence of one hundred fold (or greater) excesses of calcium and sodium?

(2) Anion exchange is less common than cation exchange in bentonites, but sulfate is known to be adsorbed. Thus, will sulfate adsorption occur sufficiently to reduce the effective cation exchange capacity of the clay?

(3) The adsorption of metal ions by bentonites is best in neutral media. In moderately acidic medium, the H^+-form of the clay is preferred. In strongly acidic or alkaline media, the clay is attacked chemically. Fortunately, this last point is not very important to us since the model mine effluent has a pH ≃ 5.4.

(4) Oxidation of the thio-species in mine effluent to sulfate results in a decrease in pH. This will, of course, affect the sorption of trace metal ions; and

(5) Very little is known concerning the state of metal ions in mine effluent. These may be present as the "aquo" ion or as thiosulfate complexes. The importance of all of these factors will have to be investigated.

RESULTS

Eight samples of Canadian bentonites available commercially were obtained from the Mineral Processing Division. From these, Aquagel (Baroid of Canada Ltd., Alberta) and Magcogel (Magcobar Mining Co., Alberta) were selected for detailed investigation on the basis of showing best results in the tests described next. X-ray diffraction analysis showed that both clays are a mixture of montmorillonite, cristobalite, quartz and a trace of feldspar.

The ion-exchange capacity of these clays was determined with ion selective electrodes to be 32.5 and 25.8 meq/100 g clay for Aquagel and Magcogel, respectively. In this method, the clays are equilibrated with a large excess of sodium or calcium ion and the released calcium and magnesium ions or sodium and potassium ions, respectively, are measured. As is generally the case with Canadian bentonites, the majority of the adsorbed ions are calcium (which occupy 23.1 and 20.8 meq/100g for Aquagel and Magcogel, respectively). Some sodium and magnesium ions are also exchangeable.

Instead of studying the behavior of bentonites in "thioacid" medium immediately, it was decided to begin with a preliminary investigation in acetate medium. Herein, a better control of the experimental conditions such as solution pH, trace metal ion hydrolysis and maintenance of a calcium ion concentration similar to that in the model mine effluent, is possible. The concentration of trace metal ion in the acetate medium was varied from approximately 0.5 to 20 ppm for Fe(II), Zn(II) and Pb(II) and from 0.02 to 20 ppm for Cu(II). In all cases, a clay suspension, 0.24% by weight, was used. Equilibration time was 18 hours. The concentration of trace metal ion not adsorbed was determined by A.A.

Trace metal ions are adsorbed to some degree by bentonites in the presence of 100 fold (or greater) excesses of calcium or sodium in acetate medium. The amounts adsorbed depend both on the metal ion (i.e., its nature and concentration) and the sample of bentonite used. As the initial concentration of metal ion decreases, the fraction adsorbed by the clay increases. The facility of adsorption decreases in the order Fe>Cu>Pb>Zn for Aquagel and Fe>Pb>Cu>Zn for Magcogel at an initial metal ion concentration, M_i of 5 ppm. As M_i becomes quite small (i.e., <1 ppm), the fraction adsorbed by the clay becomes less dependent on the nature of the metal ion. One result of considerable interest is that both Aquagel and Magcogel adsorb quantitatively Cu(II) at $M_i \leq 0.136$ ppm. Cu(II) is, of course, highly objectionable.

All the data for the acetate medium indicate that there is no relationship between the magnitude of the ion-exchange capacity and the ability of bentonite to adsorb trace metal ions. This suggests that, in future, each sample of clay must be evaluated individually in preliminary adsorption tests.

A study of bentonite clays in a synthetic "thioacid" medium is now underway. This medium contains ~220 ppm Ca^{2+}, ~590 ppm Na^{+}, ~1350 ppm SO_4^{2-} and ~680 ppm $S_2O_6^{2-}$. (1 ℓ of this medium also contains 0.25 ml glacial acetic acid to maintain the pH at approximately 5.4.) The concentration of the trace metal ions is being varied from 0.5 to 10 ppm for Fe(II),

Zn(II) and Pb(II) and from 0.02 to 10 ppm for Cu(II).

To date, Fe(II), Cu(II) and Zn(II) have been studied in the concentration range of 0.5 to 10 ppm. The data in "thioacid" medium differ only slightly from those in acetate medium. The adsorption of trace metal ions by Aquagel is a little enhanced in "thioacid" medium, whereas that by Magcogel shows a slight decrease.

It would appear at the moment that the use of Aquagel is preferable to that of Magcogel in the removal of trace quantities of metal ions. There is, of course, a great deal of work to be done but the results obtained to date look encouraging.

= = =

3.15 - REVEGETATION OF MINE WASTES

BY

T.S. Cochrane

ABSTRACT

The revegetation of mine wastes is part of the ground control program carried by the Mining Research Centre. Initiated in January 1971 the study advanced under the guidance of a full-time agronomist with part-time assistance from ground control personnel at an estimated cost of $45,000. The progress is detailed in three reports, one of which is a state-of-the-art review.

PROGRESS IN 1971

Approximately 300 million tons of ore (including coal) and waste rock are mined annually in Canada from surface workings. If the slope walls of these large excavations could be designed with the same degree of accuracy as soil slopes, and if support systems could be developed comparable to those used for underground excavations, waste volumes could ultimately be reduced, resulting in economic savings. The objectives of the Mining Research Centre's surface working project are:

1. to develop design systems suitable for open pit rock slopes;
2. to develop artificial support systems for open pit rock slopes;
3. to develop reclamation procedure for waste embankment;
4. to develop design procedures for foundations on rock.

Revegetation of mine wastes is one part of the reclamation sub-project. This study was started in January 1971 and progressed as follows:

1. a literature survey, January to March;
2. an examination of the problems associated with uranium tailings, April to May;
3. an in-depth study of the physical growth conditions and preliminary field plot tests, June to October.
4. an in-depth study of chemical growth conditions November/71 to April/72.

Literature Survey (IR MR-71/31)

The literature survey, a state-of-the-art review, although not exhaustive established the main factors to be considered in revegetation of wastes; indicated what is being done internationally; brought into focus the Canadian effort to date; and compiled an excellent bibliography of papers prepared on the subject dating from 1964-5.

Some of the more important conclusions pertaining to the Canadian scene are:

1. The revegetations of spoils in Canada is no different a problem than that found in other parts of the world.

2. Neutral non-toxic spoils like these associated with gold mining are easiest to vegetate. Banks of tailing ponds can be seeded to prevent erosion while the ponds are still functional, and the surface seeded following closure.

3. Sulphide spoils such as coal overburdens, uranium and base metal tailings present a more serious problem. However for the bulk of these spoils the addition of lime and the careful selection of plants should give satisfactory results.

4. For high sulphide spoils there is a problem of "know how". Effective methods of neutralizing have not been developed. Research is necessary to control the acidity of the waste during mining and on disposal, and to identify the special plant life that will grow on this type of spoil.

Revegetation of Uranium Tailings, Elliot Lake

In the Elliot Lake area there are ten uranium tailing areas. Two are still in operation, the other eight have been abandoned for periods varying from 1 - 12 years. The total area of the abandoned tailing ponds is estimated as 717 acres. Revegetation is needed for pollution control and aesthetic reasons.

Following examination of the wastes it was felt that although no vegetation program has been successful to date, it was a lack of technology that was hindering progress. Before large scale seeding is tried the growing conditions have to be understood and made more amenable where possible.

A two part preliminary study of growing conditions was started in May. From May to September the physical conditions affecting revegetation were identified. Data was gathered on climate, topography, surface characteristics and soil conditions. In addition two small field plots were set out on a tailing pond to gain experience in handling the tilling material as a soil and to observe the growth of 15 plant series. The results of this phase of the study are presented in an internal report (IR MR 71/104).

In November with the cooperation of the Soil Research Institute,

Ottawa, the second phase of the study, an evaluation of the chemical characteristics of tailing samples was started. This laboratory work and growth chamber tests are presently underway.

Some of the immediate problems identified from the study to date are:

- excessively high water table;
- lack of soil structure or cohesion between particles;
- inability of tailings to support agriculture equipment;
- water and wind erosion;
- debris at perimeters of tailings;
- low permeability and slow infiltration.

Recommended order of preliminary treatment is as follows:

- lower the water table and improve the drainage of the pond;
- incorporate large amounts of organic matter in any form (20 to 30 tons per acre) into the tailings;
- vegetation starting in the spring at the edges of the tailings;
- seed two or three grasses only.

BIBLIOGRAPHY

1. Murray, D., "Vegetation of Mine Waste Embankments in Canada", Internal Report MR 71/31-ID, March 1971.
2. Murray D., "Factors Affecting Revegetation on Uranium Mine Tailings in Elliot Lake Area". Part I. Physical Conditions" Internal Report MR 71/104-ID, October 1971
3. Murray, D., "Revegetation problems of mine tailings in Northern Ontario", Internal Report 71/113. Proc. of the OAC Cover Crop Committee Workshop, held November 18, 1971 at Guelph University, (to be published early 1972).

3.16 - PROGRESS WITH PROBLEMS OF COAL MINE REFUSE BANKS

presented by

T. E. Tibbetts

Environmental pollution associated with banks of refuse material built up over a long history of coal mining was brought to the attention of the Fuels Research Centre about three years ago. Two reports have been published concerned with the uncontrolled smouldering in the waste bank located on the outskirts of the town of Springhill, Nova Scotia.

The latest report, entitled, "Evaluation of Material from Springhill Coal Mine Waste Bank With a View to Reclamation" was released in January, 1971. This report included the results of an extensive drill core sampling designed to:

(1) estimate the total volume of material present in the bank and the proportion of recoverable components;

(2) indicate the future of uncontrolled combustion;

(3) develop a procedure whereby the waste material could be reclaimed and utilized with a view to at least partially offsetting the cost of extinguishing the fires and reclaiming the area for recreational or other purposes.

A major part of the study was devoted to processing the material of the bank by means of a method developed in Canada for cleaning and dewatering coal with water cyclones, screens and centrifugal driers. This separates marketable products from the waste and returns the final reject in a substantially dewatered state without thermal drying.

It was estimated that the bank contains 1.7 million tons of mineral and carbonaceous material. Parts of the bank are virtually untouched as yet by the fire and pose an air pollution threat well into the future.

Results indicate that a yield of 20 to 30 per cent coal could be expected at ash contents varying from 18 to 26 per cent.

The investigation indicated the possibility of offsetting the costs of normal control procedures by using the coal for thermal power generation.

Public agitation for action on the part of governments to eliminate this health hazard and nuisance from its midst was answered by assurances that the problem was being studied and a report was being prepared. One year following release of that report and a submission of an engineering-cost proposal to the provincial government, the latter by a private engineering company, no apparent action has been taken. This seems to offer another example of governments overlooking the intent of their own legislation.

None the less, the Fuels Research Centre is hopeful that a combination of sound technical investigation and positive economic evaluation will encourage the necessary political action to make available the necessary funds that might someday result in a clean-up of these ugly and unhealthy sites. The Fuels Research Centre is continuing to explore the potential of similar applications in other regions of Nova Scotia, particularly in Pictou County where more than three-million tons of coal mine refuse are banked and are a potential danger to the environment.

As well, inspections have been carried out at reclamation sites in the United Kingdom where coal and waste are being separated and both economically utilized, and where thousands of acres of land have been given new life.

We have been instrumental in having one of the foremost experts in this field from the United Kingdom visit Ottawa in April for the purpose of telling us about their experience over there. We hope you will all attend his lecture at the forthcoming meeting of the CIM Coal Division, April 11, 1972.

3.17.1 - THE CLEAN FUEL GAS CONCEPT IN A COMBINED GAS TURBINE-STEAM TURBINE POWER PLANT.

by

W. A. Herrmann

Several authors, among them Bennett Lewis [1) 2)] have published a number of reports, which predict that the investment for nuclear power stations will decrease in a few years from $333/kw, i.e., the Candu reactor, to about $100 per /kw, i.e., the Dresden III, and the cost per kwh will be reduced from 7.2 mills (Nine Mile Point) to about 2.52 mills in 1976. The above figures were projected in 1966 and, in the meantime, considerable doubts have arisen as to the validity of these predictions.

Besides this, nuclear plants too have pollution problems, and the above-mentioned figures do not take into account the water pollution from the extraction of the U- and Th-ores, as well as the reprocessing of the fuel elements. For a comparison of fossil and nuclear-fuelled power plants we present a proven scheme for the generation of power from the low-grade coal [3)] by gasifying the coal, which may have between 20 and 45% ash, under a pressure of 300 to 450 psi with air and steam to produce sulphur-free fuel gas of about 110 BTU/scf. As shown in Figure 1, the gas leaves the generator at about 800°F and is scrubbed with water to eliminate most of the tar and all the coal dust*, as well as alkalies and chlorine**. Simultaneously, it is cooled to about 320°F and thereby saturated with steam, which causes an expansion of the gas, thus converting the lost sensible heat into volume gain and therefore into kinetic energy in the following turbine, in which it is expanded to 140 psi. The gas volume produced is about 2.5 times the air needed to gasify the coal and this permits, besides compression of the air for the gasifier up to full pressure, the generation of up to 6% of the total energy output as electrical power. Therefore, increasing operating pressure of the gasifier increases the efficiency of the plant.

Before the fuel enters the expansion turbine it is desulphurized by scrubbing it with alkazid lye*** under full pressure, which dissolves the H_2S preferentially leaving most of the CO_2 and the hydrocarbons in the gas while taking our practically all H_2S and NH_3 [4)]. The cost of this desulphurization is about 0.538 mills/kw without any credit for sulphur. The capital cost of the desulphurization plant corresponding to $8.75/kw investment is 0.248 mills/kw. Since the coals usually contain some alkalies and chlorine, which accumulate in the scrubbing water, it is necessary to dispose of a quantity of about 3 M^3 of this water per 100 MW. This was water contains 3 g/l free NH_3, 5 g/lH_2S, 7 g/l phenols, 2 g/l fatty acids besides 50 to 70 g/l NaCl. The desulphurization of the raw fuel gas consists only of four towers (Figure 2) for

---

* To max $2/mg/m^3$

** The tar and most of the water are separated and recycled to the gasifier thus minimizing the need for waste water treatment.

*** Dimethylamineacetic acid potassium salt.

a) cooling, b) scrubbing with alkazid lye, c) stripping of the alkazid lye and d) reheating the purified gas. The investment cost of $8.75/kw in 1970 would be $13.95 in 1978. The reason for this difference in cost is that in the gasification scheme the sulphurous gas (H_2S) is absorbed in solution under pressure and at low temperature, while in the stack-gas clean-up schemes following conventional combustion the sulphurous gases (SO_2 & SO_3) are adsorbed at atmospheric pressure and at higher temperatures. In the gasification scheme the reducing gases enter the scrubbing system at about 300°F and leave at 285°F. The H_2S liberated on letting down the pressure of the scrubbing solution is burnt in a Claus Oven to elemental sulphur. The cost of removing the same quantity of sulphur from stack-gases following conventional combustion in a power plant would cost from $25/kwh[4])to $40/kwh in 1970[6]).

The purified fuel gas, reheated and saturated with steam, enters the expansion turbine at 485°F and leaves it at about 140 psi and 320°F. It then enters the two combustors of the gas turbine, in which it is burnt. In these combustors, which are simultaneously steam boilers, it generates steam at 985°F and 1910 psi for the steam turbine generator and is thereby cooled from about 2800°F to the entrance temperature of the gas turbine, about 1500°F (presently up to 1920°F is permissible), thus reducing the requirement of excess air and therefore the losses and capital cost of the gas-turbine. The off gases leave the gas turbine at about 850°F to preheat the condensate from the steam turbine, reheated by extraction steam to about 260°F, to the boiler entrance temperature of 630°F. The flue gas enters the atmosphere at about 320°F. The gas turbine produces up to 43% and the steam turbine up to 55% of the total energy output.

The investment for the prototype plant in Luenen, Germany, which has a capacity without reheat of 170 MW (See Table 1) is $111/kw in 1970[3]). This compares with a conventional plant of the same size with reheat (excluding costs for land, planning, construction supervision and interest during construction) of $137/kw[3]). The output of the gas turbine can be increased by raising the operating pressure of the gasifiers to 450 psi and by reducing the air ratio of the gas turbine, the overall output can be increased to 185 MW. This corresponds to an overall efficiency of about 40% of the heat in the fuel which reduces the investment costs to 102/kw[3]). By permitting higher combustion temperatures, the output of the gas turbine can be further increased essentially without affecting the steam turbine and efficiencies of above 40% can be reached. The cost of a 1000 MW plant of this type would be in 1978, according to the data given by the Lurgi[5]) and other authors and considering an inflation factor of 6% per year, $104.5 per kw which is composed of about $23.1 for gas generation including desulphurization + $23.0 for the gas turbine generator and $58.4 for the boiler plus steam turbine generator.

A generating unit of this type is very flexible and can be started up in less than 20 minutes from zero to full load.

The actual costs in mills per kwh are given in Table 2. This table shows that for a 1000 MW plant the generating costs will, in 1978, consist of

Table 1

Cost per kw Installed of Combined Gas-Steam Power Plants in Million $

Equipment/Size	Actual 170 MW in 1968	Estimated 363 MW in 1971	Estimated Battery Limits 1000 MW in 1971	4000 MW Thermal Plant Overall in 1971	2160 MW Nuclear Plant in 1971
Gas Generation + Cleaning	3.2	11.9	23.1		
Gas Turbine Generator	3.4	9.7	23.0		
Steam Turbine + Generator	8.7	21.2	58.4		
Total Cost Installed	15.3	42.8	104.5	746.	746.
Cost per kw installed	90. by Steag[3)]	117.7 from data of the Lurgi Co.[5)]	104.5	187.	345.

Table 2

	1000 MW Gasification Gas Turbine Steam Turbine mills/kwh	4000 MW Thermal Plant in 1971 mills/kwh	2160 MW Nuclear Plant in 1971 mills/kwh
Capital Charges	2.23	1.85	3.59
Personnel and Maintenance	0.35	0.29	0.38
Fixed Costs	2.58	2.17	3.97
Utilities	0.16		0.13 (heavy water)
Fuel Consumption* 8610 BTU/kwh	2.58 (1.64)	3.11	0.71 (fuelling)
Variable Costs	2.74	3.14	0.84
TOTAL COSTS	5.32	5.28	4.81

*At $4/ton high ash coal = 0.1905/MMBTU this figure is reduced by 0.94 mill/kw to 1.64 mill/kw and the total costs are then 4.35 mills/kw.

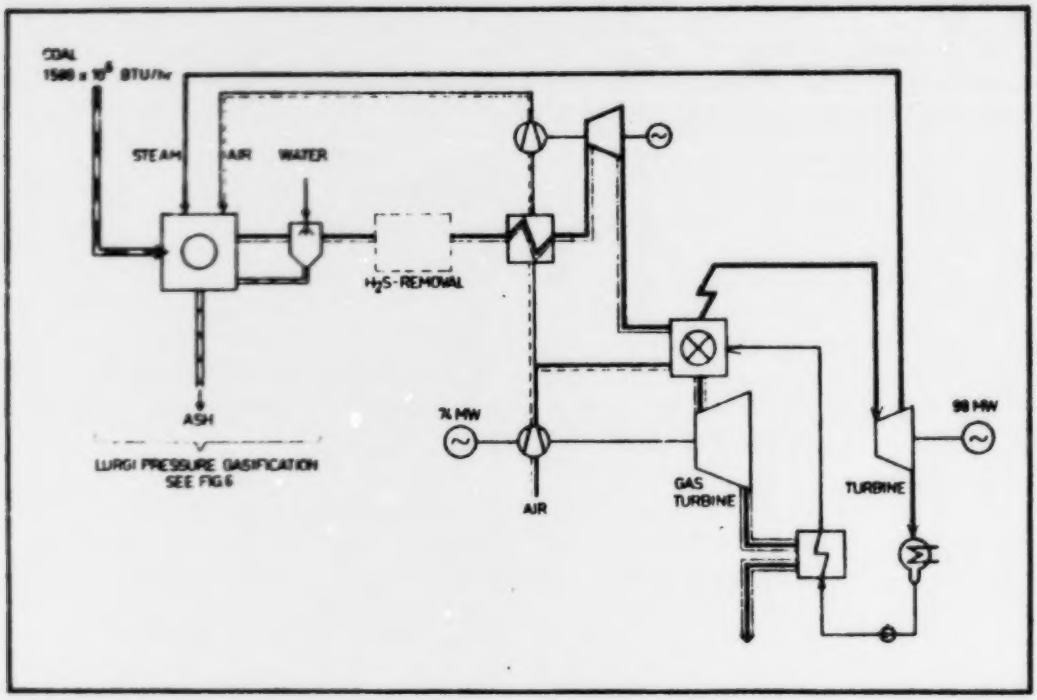


Fig. 1 Combination of Gasification with Gas Turbine Power Plant

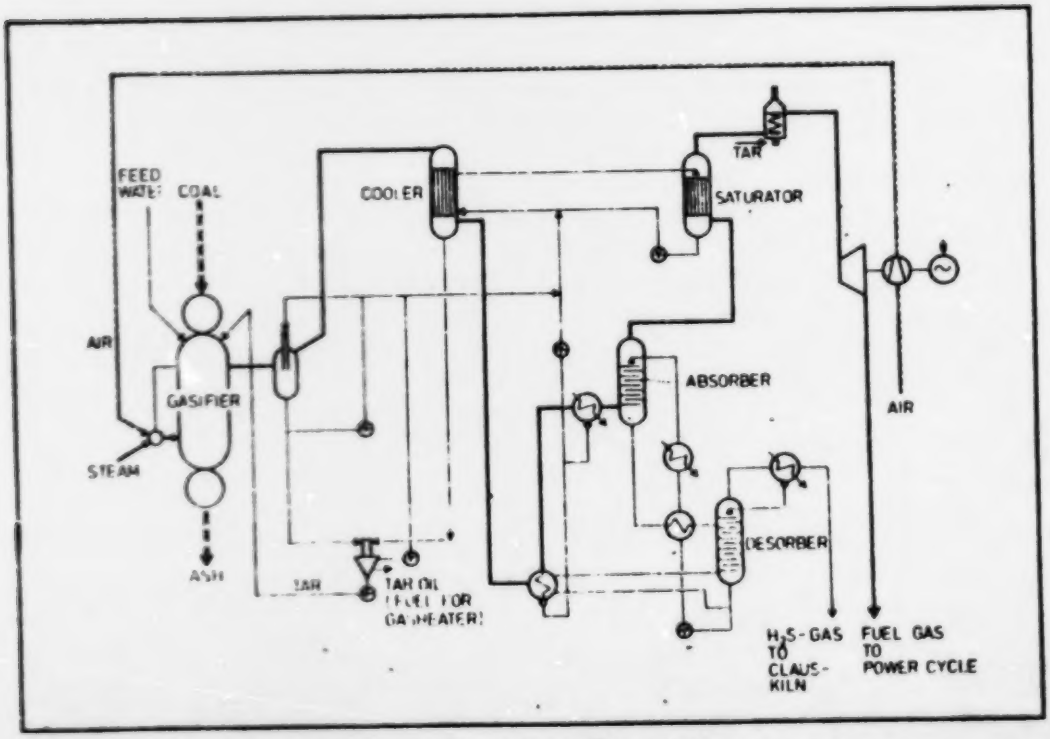


Fig. 2 Flow Sheet Clean Fuel Gas Concept

2.23 mills/kw capital charges, 0.35/mills/kw personnel and maintenance, 0.16 mills/kw utilities and 2.58 mills/kw for fuel, i.e. a total of 5.32 mills/kwh of which 41.8 % are capital costs.

REFERENCES

1) L. R. Haywood: Trends in Atomic Power Costs Revised Paper Presented at AIME Nuclear Metal Lung Symposium, Televan, Wisconsin, Oct. 3, 1966.

2) W. Bennett Lewis: Prospect of Very Low Cost Power from Ontario Hydro, Based on Large Capacity Nuclear Generating Stations, DM-112, Chalk River, Ont., Aug., 1970.

3) K. Bund, K. A. Henny, K. H. Kreb: Combined Gas-Steam Turbine Generating Plant with Bituminous Coal High Pressure Gasification Plant in the Kellerman Power Station at Luenen, paper presented at the 8th World Energy Conference in Bucharest, June 28, 1971.

4) Paul F. H. Rudolph: New Fossil Fueled Power Plant Process based on Lurgi Pressure Gasifications of Coals, paper presented at the Joint Conference of the CIC with the ACLS, May 26, 1970.

5) Clean Fuel Gas from Coal, Technical Bulletin presented by the Lurgi Gesellschaft fur Werme und Chemitechnik mbH, Frankfurt, May 1971.

6) E. V. Slack: Limestone Process for Power Plant Flue Gas Desulphurization, paper given at the Symposium on Industrial Waste Management at Sheridan Park, Ont., Nov. 3, 1971.

3.17.2 - LITERATURE REVIEW

METHODS FOR THE REMOVAL OF SULPHUR DIOXIDE FROM WASTEGASES

by

H. P. Gibbs

A critical review is presented in Mines Branch Information Circular IC 272 of processes for removing sulphur dioxide from waste gases from smelters and fossil-fuelled electrical generating stations. Over forty different methods are discussed, ranging from those in commercial operation to some under laboratory development.

3.18 - COMMITTEE ACTIVITIES

Organization for Economic Co-operative Development

(a) Joint Group on Air Pollution from Fuel Combustion

E. R. Mitchell took a leading role in the deliberations of this expert group and at its third meeting in Paris held in December 1971, he was unanimously elected by the group to serve as chairman. The committee's final report is in preparation and it is hoped to obtain approval for its publication from contributing countries by mail. If this should prove to be impossible then a final meeting will be held in Paris in April 1972. In any event the expert group's final report must be presented to the OECD's sponsoring committees in June-July 1972.

(b) Long Distance Mass Transport of Pollution

G. K. Lee is a member of this expert group and has contributed to the development of plans for aerial probing of SO_2 over the Scandinavian and central European countries. Aerial probing has commenced in Norway, but it will be sometime before direction comes from it.

ASME Research Committee on Deposits and Corrosion

G.K. Lee was invited to join this international committee and attended a meeting in Washington, D.C. on December 1, 1971. At this meeting he was appointed program chairman with responsibility for soliciting appropriate papers and arranging a technical session on fire-side corrosion and deposits at the 1972 ASME Winter Annual Meeting to be held in New York.

Industrial Waste Management Seminar

This seminar, held at Sheridan Park, Ontario was attended by G. K. Lee. Sessions were conducted on the industrial aspects of noise pollution, air pollution, meteorology, SO_2 removal and recovery systems as well as biological treatment of waste in water. Mr. Lee's main contribution was to the session on air pollution, meteorology and SO_2 removal and recovery systems.

International Field Year on the Great Lakes

The Air Pollution Task Force associated with this geophysical study held one meeting in Toronto to plan strategies for probing the mass transport of air pollutants across Lake Ontario in 1972. E. R. Mitchell and G. K. Lee are committee members.

Energy, Mines and Resources Co-ordinating Committee on Environmental Matters

E. R. Mitchell and F. T. Rabbitts represent Mines Branch on the department's Co-ordinating Committee on Environmental Matters. All matters pertaining to the department's interests in the environment are channelled through this committee which reports to the Deputy Minister. It meets bi-weekly.

Energy, Mines and Resources Urban Activities Task Group

This is an expert ad hoc task group set up by the Energy, Mines and Resources Co-ordinating Committee on Environmental Matters. G. K. Lee represented the Mines Branch on this task group and documented branch research having both direct and indirect interest to the study which will be conveyed to the Department of Urban Affairs.

NRC Associate Committee on Scientific Criteria for Environmental Quality
Sub Committee on Air

E. R. Mitchell represents Energy, Mines and Resources on this committee and attended two meetings. Research proposals have been summarized and the formation of small working groups to write criteria for particulates, SO_2 and other emissions has proved to be too time-consuming to be practical with the result that the possibility of this writing being done by consultants is being investigated.

Canadian Standards Association

(a) Committee on Air Pollution Control

E. R. Mitchell and Dr. H. Whaley each attended a meeting of the main committee which is writing standards for analytical methods and incineration.

(b) The Committee on Air Pollution Control appointed a sub-committee on Emission Sampling and Measurement and appointed Dr. H. Whaley of the CCRL to chair the sub-committee. At the same time Dr. Whaley was appointed a member of the main air pollution control committee.

(c) Committee on Incineration

F. D. Friedrich was appointed to this committee and attended two meetings which dealt with incinerator performance.

(d) 200 - Series Standards for Combustion Equipment

Several draft standards for combustion equipment were reviewed and commented upon. The large number of 200-series committees are very active and it is difficult to keep abreast of this activity.

4. DISCUSSION - NEXT SEMINAR

In a brief discussion period following the authors' presentations it was felt that the next meeting should address environmental improvement in the light of a pending energy crisis. It was also suggested that the next meeting be held at Camsell Hall to encourage wider participation.